

Phase Equilibrium Modeling in Gas Purification System

A Thesis Submitted in Partial Fulfillment for the Award of the Degree

Of

MASTER OF TECHNOLOGY

In

CHEMICAL ENGINEERING

By

Tarun Kumar Mondal



**Chemical Engineering Department
National Institute of Technology
Rourkela 769008**

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Under the guidance of

Dr. Madhushree Kundu



**Chemical Engineering Department
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May 2009



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CERTIFICATE

This is to certify that the thesis entitled “*Phase Equilibrium Modeling in Gas Purification System*”, being submitted by **Tarun Kumar Mondal** for the award of M.Tech. degree is a record of bonafide research carried out by him at the Chemical Engineering Department, National Institute of Technology, Rourkela, under my guidance and supervision. The work documented in this thesis has not been submitted to any other University or Institute for the award of any other degree or diploma.

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ACKNOWLEDGEMENT

I would like to express my appreciation to all those people who have contributed to make this work possible through their help and support along the way.

My deepest gratitude goes to my thesis supervisor Dr. Madhushree Kundu for giving me the possibility to do this interesting project and for her trustworthy advice and support through all the phases of the project. I am indebted to Dr. Madhushree Kundu for her some remarkable qualities, such as her depth of perception and her lucid presentation, perhaps the best I have come across so far, will always continue to inspire me. The experience of working with her, I strongly believe, will have far-reaching influence in my future life.

I express my gratitude and indebtedness to Professor S.K.Agarwal, Head, Chemical Engineering Department, and Professor K.C.Biswal, Ex-Head, Chemical Engineering Department, for providing me with the necessary computer laboratory and departmental facilities.

I express my immense gratitude to Professor G.K.Roy of the Department of Chemical Engineering for his valuable suggestions and encouragement. I express my gratitude and indebtedness to Dr.Basudeb Munshi, Dr. Santanu Paria, Dr. Sunil Maity of the Department of Chemical Engineering, for their valuable suggestions and instructions at various stages of the work. I would like to express my sincere gratitude to Mr. Palas Kundu of the Department of Electrical Engineering, JadavpurUniversity for his assistance and help in my computational work. I am also thankful to my friend, Pyare Mohan Pradhan for his help in computational work.

Finally, I express my humble regards to my parents, for their immense support, sacrifice and their unfettered encouragement at all stages.

TARUN KUMAR MONDAL

NATIONAL INSTITUTE OF TECHNOLOGY

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ABSTRACT

PHASE EQUILIBRIUM MODELING IN GAS PURIFICATION SYSTEM

Removal of acid gas impurities such as carbon dioxide (CO_2), carbonyl sulfide (COS), and hydrogen sulfide (H_2S) from gas streams is a very important operation for natural gas processing, oil refineries, ammonia manufacture, coal gasification, and petrochemical plants. The removal of acid gases from gas streams, commonly referred to as acid gas treating and also as gas sweetening, is a technology that has been in use industrially for over half a century. For the rational design of gas treating processes knowledge of vapour liquid equilibrium of the acid gases in alkanolamines are essential, besides the knowledge of mass transfer and kinetics of absorption and regeneration. Moreover, equilibrium solubility of the acid gases in aqueous alkanolamine solutions determines the minimum recirculation rate of the solution to treat a specific sour gas stream and it determines the maximum concentration of acid gases which can be left in the regenerated solution in order to meet the product gas specification.

Over the decades, we have witnessed a significant development in modeling vapour-liquid equilibria of acid gases over alkanolamines. Some of the path breaking works in this regard are models developed by Kent & Eisenberg (1976), Desmukh and Mather (1981), Electrolytic NRTL model by Austgen et al. (1989), and Clegg-Pitzer correlation by Li and Mather.

For the (CO_2 – MEA - H_2O), (CO_2 – DEA - H_2O) and (CO_2 – MEA - MDEA - H_2O) systems, pseudo equilibrium constant based models have been developed by considering phase and chemical equilibria for those reactive absorption processes. The vapor phase has been assumed to be ideal and vapor-liquid equilibria being guided by Henry's law. The systems considered here contain both electrolytes and non - electrolytes, the electrolyte species are partially or wholly dissociated in the liquid phase to form ionic species. However, unless the system temperature is very high, vapour phase dissociation of electrolyte components will be negligible. The ionic species do not play an important role in phase equilibrium calculations. Chemical equilibrium governs the distribution of an electrolyte in the liquid phase between its molecular and ionic forms. Since, it is the molecular form of the electrolyte that comes to equilibrium with the same component in the vapour phase, chemical equilibrium significantly affects the phase equilibrium and vice-versa. The

literature values for some of the ionization constants and Henry's law constant are adopted directly here to calculate the equilibrium partial pressure of CO_2 over alkanolamine solutions. Deprotonation of amine and carbamate reversion reaction constants were regressed using solubility data from open literature. The model developed here for a CO_2 - aqueous primary /secondary alkanolamine/ alkanolamine blend can be confidently used for predicting VLE of CO_2 over other newly proposed alkanolamine solvents and its blends as is evidenced by its excellent correlation and prediction deviation of equilibrium CO_2 partial pressure in comparison to the existing literature values.

A thermodynamic model based on activity is proposed to correlate and predict the vapour-liquid equilibria of the aforesaid systems. The activity based models render an insight in to the molecular physics of the system; hence accurate speciation of the equilibrated liquid phase becomes a reality besides its prediction ability of solubility of the acid gases over alkanolamine solutions. The activity based model has been developed using extended Debye-Hückel theory of electrolytic solution with short range, non-electrostatic interactions. The vapor phase non-ideality has been taken care of in terms of fugacity coefficient calculated using Virial Equation of State. The equilibrium constants are taken from literature as functions of temperature only. The neutral and ionic species present in the equilibrated liquid phase have been estimated with zero interaction model and incorporated here. The interaction parameters in the activity models are estimated by minimizing the objective function, which is the summation of relative deviation between the experimental and model predicted CO_2 partial pressures over a wide range.

The parameter estimation for the phase equilibrium models have been formulated here as a multivariable optimization (minimization) problem with variable bounds. The MATLAB 7.6 optimization toolbox has been used extensively for the present work. '*fmincon*' function, which is a constrained optimization function uses quasi-Newton and Sequential Quadratic Programming (SQP) methods, has been used here for minimization of the proposed objective functions with variable bounds for both approximate and rigorous modeling. There remains a necessity of refinement of the developed rigorous thermodynamic model in terms of the accurate speciation, i.e., exact determination of the species concentration in the equilibrated liquid phase and use of better optimization algorithm, may be non-traditional one, which will ensure global minima.

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NOMENCLATURE

Uppercase Latin symbols

<i>Symbol</i>	<i>Meaning</i>
A	Debye-Huckel limiting slope
B_1, B_2	constants in equations (4.24) and (4.25)
B_{ii}	interactions between pairs of molecules
C_1-C_5	constants in equation (4.1) and Table 3.1 & 4.1
G	total Gibbs free energy
\vec{G}	vector function
F	objective function for regression
H	hessian matrix
H_0	symmetric positive definite matrix
H_{CO_2}	Henry's constant for CO_2 , kPa
I	identity matrix
I	ionic strength, mol/lit
K_i	thermodynamic chemical equilibrium constant of component i based on molarity, molality or mol fraction scale
K_m	thermodynamic chemical equilibrium constant based on molarity scale
K_x	thermodynamic chemical equilibrium constant based on mol fraction scale
M_i	molar concentration, $kmol/m^3$
M_s	molecular weight of solvent
P	total pressure, kPa
P_R	critical pressure
P_C	reduced and pressure

R	universal gas constant, 8.314 kJ/ kmol-K
T_R	reduced temperature
T_C	critical temperature
T	temperature, K

Lowercase Latin symbols

<i>Symbol</i>	<i>Meaning</i>
a_i	activity of component i
b	constant
c	constant vector
f	objective function of optimization techniques
f_i^0	fugacity of component i at some chosen reference state
\hat{f}_i	fugacity of component i in solution
\hat{f}_i^v	fugacity of component i in vapour mixture
\hat{f}_i^l	fugacity of component i in liquid mixture
m	values of the equality and inequality constraints
m	molar concentration of alkanolamine solution
m_1	molar concentration of alkanolamine solution
m_2	molar concentration of alkanolamine solution
m_t	total molal concentration of alkanolamine solution
n	number of component
p_i^{exp}	experimental partial pressure, kPa
p_i^{cal}	calculated partial pressure, kPa
P_{CO_2}	partial pressure of carbon dioxide, kPa

s_k	step length parameter
q_k	line search parameter
w_i	weight fraction of i, grams i / total grams soln
x_i	mol fraction of component i
x	design parameter
x^*	optimal solution point
x_l	lower bound parameter
x_u	upper bound parameter
y_{CO_2}	vapour phase mole fraction of CO ₂
z_i	charge number on the ion

Greek symbols

<i>Symbol</i>	<i>Meaning</i>
α	liquid phase loading of CO ₂ , mol CO ₂ / mol amine
β_{ij}	interaction parameters, kg/mol
γ_i	symmetric activity coefficient of component i
∂	partial derivative
λ_i	lagrange multipliers
μ	chemical potential
μ_i^0	chemical potential at chosen reference state
ρ	density, kg·m ⁻³
Φ_{CO_2}	fugacity coefficient of CO ₂
ω	acentric factor

Abbreviations

Abbrev.	Meaning
AAD	average absolute deviation
AMP	2-amino-2-methyl-1-propanol
BFGS	Broyden, Fletcher, Goldfarb and Shanno
DEA	diethanolamine
DGA	diglycolamine
DIPA	diisopropanolamine
MEA	monoethanolamine
MDEA	N-methyldiethanolamine
MW	molecular weight
PE	2-piperidineethanol

Chapter 1

INTRODUCTION TO GAS TREATING PROCESS

Chapter 1

INTRODUCTION TO GAS TREATING PROCESS

1.1 GENERAL BACKGROUND

Removal of acid gas impurities such as carbon dioxide (CO₂), carbonyl sulfide (COS), and hydrogen sulfide (H₂S) from gas streams is a very important operation for natural gas processing, oil refineries, ammonia manufacture, coal gasification, and petrochemical plants. The removal of acid gases from gas streams, commonly referred to as acid gas treating and also as gas sweetening, is a technology that has been in use industrially for over half a century. CO₂ and H₂S concentrations in the sour gas streams may vary widely, from several parts per million to 50% by volume of the gas streams. These impurities when present in the gas streams may lead to very serious problems in pipeline transportation and downstream processing of the gas. Some of the CO₂ is often removed from natural gas because at high concentrations it reduces the heating value of the gas and it is costly to compress this extra volume for pipeline transportation of natural gas.

The CO₂ specification is less severe e.g., less than 1 % for pipeline natural gas, 10 ppm for ammonia synthesis to prevent catalyst poisoning and 100 ppm for LNG manufacture to avoid freezing up in the cryogenic heat exchanger

(Astarita *et al.*, 1983). Cleanup targets play an important role in the selection of the gas treating processes. Astarita *et al.* (1983) provided a comprehensive summary of major industrial gas treating processes and common cleanup targets.

1.2 GAS TREATING

1.2.1 General Gas Treating Process and Major Alkanolamines

Among the most widely practiced gas treating processes, absorption into physical solvents or chemical solvents, and hybrid solvents (blends of chemical and physical solvents) are the major ones (Astarita, 1983).

Approximately 90% of the acid gas treating processes in operation today uses alkanolamine solvents because of their versatility and their ability to remove acid gases to very low levels. There are three major categories of alkanolamines; primary, secondary and tertiary. The most commonly used alkanolamines are the primary amine monoethanolamine (MEA), the secondary amines diethanolamine (DEA), and diisopropanolamine (DIPA) and the tertiary amine methyldiethanolamine (MDEA). One important class of amines is the sterically hindered amines, e.g., 2-amino-2-methyl-1-propanol (AMP), 2-piperidineethanol (PE).

1.2.2 Alkanolamine Processes

1.2.2.1 Process types

Chemical absorption processes for gas treating may be divided into three conceptual categories distinguished by the rate at which the solvent reacts with CO₂. The first group of processes can be termed “bulk” CO₂ treating processes, and are distinguished by their ability to remove CO₂ to very low levels. Bulk

removal depends on the faster reacting solvents available, primary and secondary alkanolamines and promoted hot carbonate salts. Promoted hot carbonate processes are widely used for bulk CO₂ removal where clean gas specifications are not stringent and the partial pressure of CO₂ is moderately high (Astarita *et al.*, 1983). Aqueous primary or secondary alkanolamines are generally employed for bulk CO₂ removal when the partial pressure of CO₂ in the feed is relatively low and/or the required product purity is high. Though the reaction of CO₂ with these amines is fast, it is accompanied by a highly exothermic heat of reaction (Kohl and Nielsen, 1997), which must be supplied in the regenerator to regenerate the solvent. Consequently, these processes can be energy intensive (Astarita *et al.*, 1983).

The second group of processes employing tertiary or hindered alkanolamines to avoid the faster carbamate formation reaction represents the second group of “selective” treating processes. These selective processes are capable of passing as much as 90% of the CO₂ in the feed gas while removing H₂S to very low levels (less than 4 ppm) (Kohl and Nielsen, 1997). In selective gas treating applications (such as for gas processing plants with a sulfur recovery unit (SRU)) CO₂ removal below certain limits is undesirable, since it results in higher than necessary circulation rates and reboiler steam requirements, and lower H₂S partial pressure for the SRU. In order to save energy in these applications, the tertiary alkanolamine MDEA was proposed for use as a selective treating agent. Hence, over the years MDEA has become known as a solvent providing good selectivity for H₂S in the presence of CO₂ (Kohl and Nielsen, 1997).

A third category of processes has recently grown out of the selective treating category. The use of blended amine solvents in gas treating processes is of increasing interest today. A mixed amine solvent, which is an aqueous blend of a primary or secondary amine with a tertiary amine, combines the higher equilibrium capacity of the tertiary amine with the higher reaction rate of the primary or secondary amine and can bring about considerable improvement in gas absorption and great savings in regeneration energy requirements. Blended

amine solvents are less corrosive, and require lower circulation rates to achieve the desired degree of sweetening. Since the regeneration section costs at least 50 % of the total capital cost (Sigmund *et al.*, 1981) and that steam cost makes 70 % of the variable costs (Astarita *et al.*, 1983), any small improvement in this area will translate into considerable financial savings. These solvents are better known as blended amine solvents. Since sterically hindered amine (SHA) e.g. AMP, provides as high an equilibrium capacity (1 mol of CO₂/mol of amine) as MDEA for CO₂, a primary or secondary SHA is also considered a potential component of blended amine solvents for the hybrid processes. By judiciously adjusting the relative compositions of the constituent amines, the blended amine solvents (with a much larger amount of the tertiary or sterically hindered amine and very small amount of the primary or secondary amine or even without that) can also become very good solvents for selective removal of H₂S in the presence of CO₂ in the gas streams.

1.2.2.2 Characteristics of solvents

The mutual solubilities of solvents and hydrocarbons are a function of the molecular structure of the alkanolamines and their concentrations. The larger the number of hydroxyl groups, the higher is the water solubility of the solvent and lower is the hydrocarbon solubility. The presence of more aliphatic groups tends to raise hydrocarbon solubility and lower water solubility (Butwell *et al.*, 1982). The amine group in the solvent molecules provides the basicity. DEA-based solvents have been used to process 47 % of the treated gas volume while MEA and MDEA were used to process 23% and 17%, respectively (Carey *et al.*, 1991). Historically DEA and MEA primarily have dominated acid gas treating applications. A smaller number of plants use DGA and DIPA.

The degradation products of DEA are much less corrosive than those of MEA. As a secondary amine, DEA has a reduced affinity for CO₂ and H₂S. The

heat of reaction of DEA with CO₂ is about 1477 J/g CO₂, which is 25 % less than that of MEA (Polasek *et al.*, 1985).

Unlike the primary and secondary amines, the CO₂ absorption into MDEA can reach 1 mol CO₂ per mol of amine. While the high CO₂ loading in MDEA is very attractive, the low rates of absorption of CO₂ in tertiary amines may limit their use because of the high cost of MDEA relative to MEA and DEA. In aqueous solutions tertiary amines promote the hydrolysis of CO₂ to form bicarbonate and protonated amine. Amine promoted hydrolysis reactions is much slower than the direct reaction of primary and secondary amines with CO₂ and therefore kinetic selectivity of tertiary amines towards CO₂ is poor. MDEA is kinetically selective for H₂S in the presence of CO₂. The heat of reaction associated with the formation of bicarbonate ion is much lower than that associated with carbamate formation. Thus regeneration cost for tertiary amines are lower than for primary and secondary amines.

Sterically hindered amines, e.g., 2-amino-2-methyl-1-propanol, AMP, are said to approach the stoichiometric loading of 1 mol CO₂ per mol of amine combined with the absorption rate characteristic of primary and secondary amines. This high loading is obtained by destabilizing the carbamate due to the presence of bulky substituent next to the nitrogen atom of the amine group. Sterically hindered amines have the advantage of exhibiting highly reversible kinetics with CO₂ and thus requiring less energy for regeneration. Besides saving energy and capital in gas treating processes significantly, the hindered amines have much better stability than conventional amines, since hindered amines have low or no amine degradation.

In order to combine the advantages of both physical and chemical solvents, hybrid solvents have been proposed for effectively treating acid gases. This combination allows for a higher CO₂ loading, a lower solution circulation rate and regeneration energy. In a hybrid solvent the chemically reactive alkanolamine ensures low residual levels of CO₂ even at relatively low total pressure, while the physical solvent component makes possible not only the removal of mercaptans and other organic impurities to low levels, but also the

removal of part of the CO_2 with only small heat effects during absorption and regeneration.

1.3 VAPOUR – LIQUID EQUILIBRIUM

Both, the acid gas in the liquid phase and alkanolamines are weak electrolytes. As such they partially dissociate in the aqueous phase to form a complex mixture of nonvolatile or moderately volatile solvent species, highly volatile acid gas (molecular species), and non-volatile ionic species. The equilibrium distribution of these species between a vapour and liquid phase are governed by the equality of their chemical potential among the contacting phases. Chemical potential or partial molar Gibbs free energy is related to the activity coefficient of the species through partial molar excess Gibbs free energy. An activity coefficient model (or excess Gibbs energy model) is an essential component of VLE models. The main difficulty has been to develop a valid excess Gibbs energy function, taking into consideration interactions between all species (molecular or ionic) in the system.

For the rational design of gas treating processes knowledge of vapour liquid equilibrium of the acid gases in alkanolamines are essential, besides the knowledge of mass transfer and kinetics of absorption and regeneration. Moreover, equilibrium solubility of the acid gases in aqueous alkanolamine solutions determines the minimum recirculation rate of the solution to treat a specific sour gas stream and it determines the maximum concentration of acid gases which can be left in the regenerated solution in order to meet the product gas specification. One of the drawbacks of the conventional equilibrium stage approach to the design and simulation of absorption and stripping is that, in practice absorbers and strippers often do not approach equilibrium conditions. A better approach to design such non-equilibrium processes (mass transfer operation enhanced by chemical reaction) is by the use of mass and heat transfer

rate based models (Hermes and Rochelle, 1987; Sivasubramanian *et al.*, 1985; Rinker, 1997). However, phase and chemical equilibria continue to play important roles in a rate-based model by providing boundary conditions to partial differential equations describing mass transfer coupled with chemical reaction. Accurate speciation of the solution is an integral part of the equilibrium calculations required by the rate-based models. Therefore a robust thermodynamic model at all possible combination of temperature, amine concentration, and acid gas loading is needed.

Solubilities of CO₂ have been reported over wide ranges of temperature, solution loadings with respect to CO₂ and amine concentrations, but the majority of the data are crowded in the middle loading range. There is a need for all the available data to be correlated in terms of a comprehensive model of the solution thermodynamics so that the solubility predictions can be confidently made where data do not exist or where they are of poor quality.

Besides, the availability of a thermodynamic rigorous model can result in the reduction of the experimental efforts required to characterize the VLE behaviour of newer solute-solvent systems, for which no data have been reported.

1.4 OBJECTIVES OF THE PRESENT WORK

The primary objectives of this work is to develop apparent and rigorous thermodynamic models to represent the VLE of CO₂ in aqueous single and blended alkanolamines and validate the models with the help of the experimental results available in the open literature over a wide range of CO₂ loading, CO₂ partial pressure and temperature.

Chapter 2

THERMODYNAMICS AND PREVIOUS WORK

Chapter 2

THERMODYNAMICS AND PREVIOUS WORK

2.1 INTRODUCTION

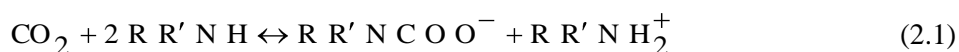
The thermodynamic concepts are essential for the development of the model to represent vapour - liquid equilibrium of CO_2 in aqueous alkanolamine solutions. This chapter provides a brief review of the chemical reactions in the CO_2 – alkanolamine systems and the relations between chemical potential, fugacity, activity coefficient and excess Gibbs energy functions, especially as they are related to weak electrolyte systems. Equilibrium thermodynamics here is the combination of physical vapour - liquid equilibrium (VLE) of molecular species and chemical reaction equilibrium that typically occur in aqueous alkanolamine systems.

A review of previous work on the modeling (apparent and rigorous thermodynamic models) the VLE of CO_2 in single and blended alkanolamines are presented here.

2.2 CO₂-ALKANOAMINE REACTIONS

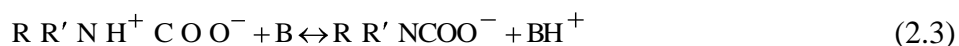
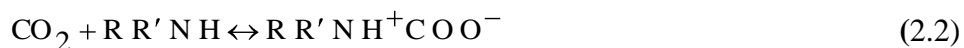
The amine group present in the alkanolamine provides the basicity whereas the hydroxyl group increases the solubility, thus reducing the vapour pressure of aqueous alkanolamine solutions.

Carbamate formation reaction:



$\text{R}' = \text{H}$ for primary amines

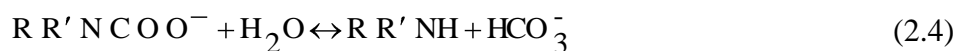
The zwitterion mechanism originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979) is generally accepted as the reaction mechanism for reaction (2.1).



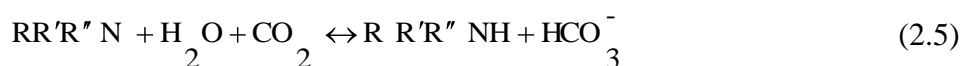
This mechanism comprises two steps: formation of the CO₂-amine zwitterion (reaction (2.2)), followed by base catalyzed deprotonation of this zwitterion (reaction (2.3)). Here B is a base, which could be amine, OH⁻, or H₂O (Blauwhoff *et al.*, 1984). However, Versteeg and van Swaaij (1988) argued that, for aqueous amine solutions, the contribution of the hydroxyl ion is minor due to its low concentration, and may be neglected without a substantial loss of accuracy. The equilibrium loading capacities of primary and secondary alkanolamines are limited by stoichiometry of reaction (2.1) to 0.5 mol of CO₂/mol of amine. For normal primary and secondary amines e.g. MEA, DEA, etc the carbamates formed (reaction (2.1)), are quite stable.

Carbamate reversion reaction:

If the amine is hindered, the carbamate is unstable and it may undergo carbamate reversion reaction as follows (Sartori and Savage, 1983):



Reaction (2.4) means that for the hindered amines one mol of CO₂ is absorbed per mol of amine. However, a certain amount of carbamate hydrolysis (reaction (2.4)) occurs with all amines so that even with MEA and DEA the CO₂ loading may exceed 0.5, particularly at high pressures and higher contact times (Sartori and Savage, 1983).

CO₂ - tertiary amine reaction:

Tertiary amines cannot form carbamates and therefore they act as chemical sink for CO₂ in aqueous solutions simply by providing basicity, the final product being bicarbonate. Hence, the stoichiometry of the CO₂ - tertiary amine reactions is 1 mol of CO₂ per mol of amine.

2.3 CONCENTRATION SCALES

Concentration is a very important property of mixtures, because it defines the quantitative relation of the components. In solutions the concentration is expressed as the mass, volume, or number of moles of solute present in proportion to the amount of solvent or of total solution. Before developing the model for the VLE of the aqueous alkanolamine-acid gas system, a concentration basis must be chosen. One difficulty that is encountered in modeling these

systems is that experimental data exists in three different concentration units, mol fraction, molality, and molarity. Therefore relationships are needed to convert between the different concentration bases. The model used here is developed using molarity and molality concentrations.

2.3.1 Molality, Molarity, Mol Fraction and Their Inter Conversations

Molality (mol/kg, molal, or m_i) denotes the number of moles of solute per kilogram of *solvent* (not solution). The mole fraction x_i , (also called molar fraction) denotes the number of moles of solute as a proportion of the total number of moles in a solution. Molarity (in units of mol/L, molar, or M_i) or molar concentration denotes the number of moles of a given substance per liter of solution.

$$x_i = \frac{m_i * MW_{Solv} * 1 \text{ kg}}{1000 \text{ g}} \quad (2.6)$$

Assuming the solvent is water, equation (2.6) becomes

$$x_i = \frac{m_i * 18}{1000} \quad (2.7)$$

First the weight fraction, w_i , of the alkanolamine is calculated from equation (2.8).

$$w_i = \frac{M_i * MW_i}{\rho_{soln} * 1000} \quad (2.8)$$

Where, w_i is the weight fraction of i , grams i / total grams soln

M_i is the molarity of component i , mol i / L soln

MW_i is the molecular weight of component i grams i / g mol i

ρ_{soln} is the density of the solution, grams solution / mL soln

To convert weight fraction to mol fraction one has to assume that amine and water are the only important species. This is usually possible since the experimental data is reported as a function of the unloaded amine-water concentration even at very high acid gas loadings. Equation (2.9) is used to convert weight fraction to mol fraction.

$$x_i = \frac{\frac{w_i}{MW_i}}{\left(\frac{w_i}{MW_i}\right) + \left(\frac{1-w_i}{18}\right)} \quad (2.9)$$

2.4 CONDITIONS OF EQUILIBRIUM

In a chemical process, equilibrium is the state in which the chemical activities or concentrations of the reactants and products have no net change over time. Usually, this would be the state that results when the forward chemical process proceeds at the same rate as their reverse reaction. The reaction rates of the forward and reverse reactions are generally not zero but, being equal; there are no net changes in any of the reactant or product concentrations.

Neglecting surface effects and gravitational, electric and magnetic fields, at thermal and mechanical equilibrium we expect the temperature and pressure to be uniform throughout the entire homogeneous closed system. Gibbs showed that at chemical equilibrium each species must have a uniform value of chemical potential in all phases between which it can pass. These conditions of phase equilibrium for the closed heterogeneous system can be summarized as:

$$\begin{aligned}
 T^1 &= T^2 = \dots T^n \\
 P^1 &= P^2 = \dots P^n \\
 \mu_i^1 &= \mu_i^2 = \dots \mu_i^n
 \end{aligned}
 \quad i = 1, 2, \dots, m
 \quad (2.10)$$

Where n is the number of phases and m is the number of species present in the closed system. μ_i is defined by the equation (2.13).

$$\mu_i = \left(\partial G / \partial n_i \right)_{T, P, n_{j \neq i}} \quad (2.11)$$

G is the Gibbs free energy of the open system (phase) and n_i is the number of moles of component i .

2.5 CHEMICAL EQUILIBRIA AND PHASE EQUILIBRIA

In a closed vapour - liquid system containing both electrolytes and non - electrolytes, the electrolyte species will partially or wholly dissociate in the liquid phase to form ionic species. However, unless the system temperature is very high, vapour phase dissociation of electrolyte components will be negligible. This suggests that, in practice, it is necessary to apply equation (2.10) only to neutral molecular species to determine the equilibrium distribution of components between the vapour and liquid phases. Because ions will be present only in the liquid phase for applications of interest in this work, equation (2.10) can be neglected for ionic species. This is not to suggest that ionic species do not play an important role in phase equilibrium calculations. Chemical equilibrium governs the distribution of an electrolyte in the liquid phase between its molecular and ionic forms. Since, it is the molecular form of the electrolyte that comes to equilibrium with the same component in the vapour phase, chemical equilibrium significantly affects the phase equilibrium and vice-versa.

Both acid gases and alkanolamines may be considered weak electrolytes in solution, thus they dissociate only moderately in a binary aqueous system. However, in a mixture the chemical reactions, all forming ionic species as products, may lead to a high degree of dissociation resulting in a high ionic strength of the solution. The high molar concentrations and high ionic strengths lead to an expected non-ideal behavior of the liquid phase resulting from long-range ionic interactions and short range molecular interactions between species in solution.

Chemical potential is a difficult thermodynamic variable to use in practice, partly because only relative values of this variable can be computed. Moreover, as the mol fraction of a component approaches infinite dilution, its chemical potential approaches negative infinity. To overcome these difficulties, G.N. Lewis (Lewis and Randal, 1961) defined a new thermodynamic variable called fugacity. f_i , which he related to the chemical potential as

$$\mu_i - \mu_i^0 = RT \ln \hat{f}_i / f_i^0 \quad (2.12)$$

Where μ_i^0 and f_i^0 are arbitrary, but not independent, values of the chemical potential and fugacity of component i for some chosen reference state. \hat{f}_i is the value of the fugacity of component i in the mixture. The difference in chemical potential $\mu_i - \mu_i^0$, is written for an isothermal change between the arbitrary reference state and the actual state for any component in the system. The ratio \hat{f}_i / f_i^0 is called the activity of the species i , ' a_i .' Lewis was able to show from equations (2.10) and (2.12) that an equivalent and more conveniently applicable, expression of phase equilibrium for all species at constant and uniform values of the system temperature and pressure is

$$f_i^1 = f_i^2 = \dots f_i^n \quad i = 1, 2, \dots, m \quad (2.13)$$

Equation (2.13) has been widely adopted for phase equilibrium calculations. However the concept of chemical potential continues to be used in chemical literature, specially as it relates to chemically reactive systems including electrolyte systems. Indeed, because of its relation to Gibbs free energy, chemical potential is the thermodynamic variable generally manipulated to determine the equilibrium distribution of species in a chemically reacting system at constant temperature and pressure. Both the phase and chemical equilibrium must be considered. Fugacity coefficient and activity coefficient are the two important variables in vapour phase and liquid phase thermodynamics.

2.6 IDEAL SOLUTIONS, NON-IDEAL SOLUTIONS AND THE ACTIVITY COEFFICIENT

A solution is defined to be ideal if the chemical potential of every species in the solution is a linear function of the logarithm of its mol fraction. That is for every component in an ideal solution the following relation holds:

$$\mu_i = \mu_i^0 + R T \ln x_i \quad (2.14)$$

Where μ_i^0 is known as standard state or reference state chemical potential of component i. μ_i^0 depends on the reference state temperature and pressure. Both Raoult's law and Henry's law can be derived from equations (2.12) and (2.14) assuming that the vapour phase behaves as an ideal gas. For a real solution, the chemical potential is not a linear function of the logarithm of the mol fraction. In order to preserve the form of equation (2.14) for real solutions, the activity coefficient γ_i , is defined such that

$$\mu_i = \mu_i^0 + R T \ln x_i \gamma_i \quad (2.15)$$

Where, γ_i is a function of temperature, pressure, and composition of the solution. It is emphasized that equation (2.15) should be viewed as a definition of the activity coefficient. Comparing equations (2.12) and (2.15), it can be seen that

$$\gamma_i = \hat{f}_i / x_i f_i^0 = a_i / x_i \quad (2.16)$$

The definition of activity coefficient from equation (2.16) is incomplete until a reference state is specified and thus a value of μ_i^0 . This can be accomplished by identifying the conditions of temperature pressure and composition at which γ_i becomes unity. μ_i^0 is then the chemical potential of component i at the conditions at which γ_i is taken, by convention, to be unity.

2.7 STANDARD STATE CONVENTION

The process of identifying reference or standard states at which the activity coefficients of all species in a solution becomes unity is referred to as normalization.

2.7.1 Normalization Convention I

By Normalization Convention 1, the activity coefficient of each component approaches unity as its mol fraction approaches unity at the system temperature and system reference pressure. That is for all components

$$\mu_s = \mu_i^0 + RT \ln x_i \gamma_s \quad (2.17)$$

$$\gamma_s \rightarrow 1 \quad \text{as} \quad x_s \rightarrow 1 \quad (2.18)$$

Since this normalization convention holds for all components of a solution, it is known as the symmetric normalization convention; activity coefficients normalized in this manner, are said to be symmetrically normalized. This convention leads to Raoult's law and applied when all components of the solution are liquid at system temperature and pressure.

2.7.2 Normalization Convention II

The reference state for the solvent is different from the reference state for the solutes adopted under Convention II. For the solvent, the reference state is the same as that adopted under Normalization Convention I. The reference state for a solute is taken to be the hypothetical state of pure solute found by extrapolating its chemical potential from infinite dilution in solvent to the pure solute (Denbigh, 1981) at the solution temperature and reference pressure. It is sometimes referred to as the ideal dilute reference state. For a binary solution, Convention II leads to the following expressions for chemical potentials and activity coefficients.

$$\mu_s = \mu_s^0 + R T \ln x_s \gamma_s \quad \gamma_s \rightarrow 1 \quad \text{as } x_s \rightarrow 1 \quad (2.19)$$

$$\mu_i = \mu_i^0 + R T \ln x_i \gamma_i^* \quad \gamma_i^* \rightarrow 1 \quad \text{as } x_i \rightarrow 0 \quad (2.20)$$

Where, the subscripts i and s refer to solute and solvent respectively. Since solute and solvent activity coefficients are not normalized in the same way, Convention II is known as the unsymmetric normalization convention. The superscript, *, on the activity coefficient of the solute is used to indicate that the activity coefficient of this solute approaches unity as its mol fraction approaches zero. This normalization convention leads to Henry's law and is applicable when some components of the solution are gases or solids at the system temperature and pressure.

2.7.3 Normalization Convention III

The concentration of solutes including salts and gases are often measured on molality scale. Accordingly, activity coefficients of these species are also often defined with reference to the molality scale. According to the Normalization Convention III, the activity coefficient of solute and solvent for a binary solution is defined as

$$\mu_s = \mu_s^0 + RT \ln x_s \gamma_s \quad \gamma_s \rightarrow 1 \quad \text{as } x_s \rightarrow 1 \quad (2.21)$$

$$\mu_i = \mu_i^\Delta + RT \ln m_i \gamma_i^\Delta \quad \gamma_i^\Delta \rightarrow 1 \quad \text{as } m_i \rightarrow 0 \quad (2.22)$$

μ_s^0 is the chemical potential of the pure solvent at the system temperature and reference pressure. μ_i^Δ is the chemical potential of the solute in a hypothetical solution of unit molality (Denbigh, 1981). That is, μ_i^Δ is the chemical potential of the solute in a hypothetical ideal solution when m_i and γ_i^Δ are both equal to unity.

2.8 CHEMICAL EQUILIBRIUM

2.8.1 Relation Between the Equilibrium Constants Based on the Mole Fraction Scale and the Molality Scale.

Considering the dissociation reaction of CO_2 into water, if the concentrations and activity coefficients are expressed in terms of the mole fraction scale in accordance with Convention II, we can write,

$$K_{x,\text{CO}_2} = \frac{x_{\text{H}_3\text{O}^+} x_{\text{HCO}_3^-} \gamma_{\text{H}_3\text{O}^+}^* \gamma_{\text{HCO}_3^-}^*}{x_{\text{H}_2\text{O}} x_{\text{CO}_2} \gamma_{\text{H}_2\text{O}}^* \gamma_{\text{CO}_2}^*} \quad (2.23)$$

The super script * on the activity coefficients of the solutes indicate that they are based on the mole fraction scale and they approach unity as the corresponding mole fraction of each solute approaches zero. The activity coefficient of water approaches unity as its mole fraction approaches unity. Similarly if the concentrations and activity coefficients are based on the molality scale in accordance with Convention III, we can write,

$$K_{m,CO_2} = \frac{m_{H_3O^+} m_{HCO_3^-} \gamma_{H_3O^+}^{\Delta} \gamma_{HCO_3^-}^{\Delta}}{m_{H_2O} m_{CO_2} \gamma_{H_2O} \gamma_{CO_2}^{\Delta}} \quad (2.24)$$

The super script Δ on the activity coefficients of the solutes indicate that they are based on the molality scale and they approach unity as the corresponding mole fraction of each solute approaches zero.

The relation between K_x and K_m for dissociation reaction of CO_2 reaction can be found most easily at the infinitely dilute state where all the activity coefficients in equation (2.23) and (2.24) are defined to be unity. For dilute solution using the relation between molality and mol fraction, it can be shown that

$$(2.25)$$

$$(2.26)$$

While equations (2.25) and (2.26) were derived for an infinitely dilute aqueous solution of CO_2 , they hold for all finite CO_2 concentrations. Similar reactions can be derived for all other reactions. The temperature dependence of equilibrium constant is often reported as

$$\ln K = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T \quad (2.27)$$

The coefficients C_1 through C_4 for different reactions are taken from different literature sources.

2.9 PREVIOUS WORK

Classical thermodynamics provides a framework for calculating the equilibrium distribution of species between a vapour and liquid phase in a closed system through the equality of their chemical potential among the contacting phases. In this regard, both apparent and rigorous thermodynamic models have been proposed by various researchers to correlate and predict the vapour-liquid equilibrium of CO_2 in aqueous alkanolamines. For the rational design of gas treating processes vapour-liquid equilibrium data of CO_2 over aqueous alkanolamines are essential besides the mass transfer and rate of chemical kinetics.

2.9.1 Approximate Thermodynamic Models

Kent and Eisenberg (1976) modified the Danckwerts/McNeil approach by tuning two of the equilibrium constants in order to make a fit to published vapor liquid equilibrium data for $\text{CO}_2/\text{H}_2\text{S}/$ amine/water systems for the amines MEA and DEA. No ionic strength dependence was considered and the value of the amine protonation constant and the carbamate reversion constant were treated as adjustable parameters and fitted to functions only of temperature. All other equilibrium constants were used at their infinite dilution value as reported in the literature.

The Kent & Eisenberg model has been adopted by several other researchers due to its simplicity and good ability to correlate experimental data with reasonable accuracy. Jou *et al.* (1982) adjusted the value of the amine protonation constant and included a dependence of acid gas loading and amine molarity to fit their experimental data for the system $\text{CO}_2/\text{H}_2\text{S}/\text{MDEA}/\text{H}_2\text{O}$. Hu and Chakma (1990) used a similar procedure to correlate their VLE data for $\text{CO}_2/\text{AMP}/\text{H}_2\text{O}$ system.

Li and Shen (1993) successfully correlated their data for the $(\text{CO}_2+\text{MDEA}+\text{MEA}+\text{H}_2\text{O})$ system by the Kent & Eisenberg approach. The chemical equilibrium constants involving alkanolamines are expressed as function of temperature, amine concentration and carbon dioxide loading over the temperature range from 40 - 100 $^{\circ}\text{C}$ and CO_2 partial pressure of up to 2000kPa

Park *et al.* (2002) used the modified Kent & Eisenberg model to determine the deprotonation constant and carbamate reversion constants for aqueous $(\text{CO}_2 + \text{MEA})$, $(\text{CO}_2 + \text{DEA})$ and $(\text{CO}_2 + \text{AMP})$ solutions at different temperatures (40 $^{\circ}\text{C}$, 60 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$) and partial pressure range of 0.1 to 50 psia.

Klyamer and Kolesnikova (1972) develop one average activity coefficient based model to correlate $(\text{CO}_2+\text{alkanolamine}+\text{H}_2\text{O})$ system. Lee and Mather (1976) correlated $(\text{CO}_2+\text{MEA}+\text{H}_2\text{O})$ system data over a wide range of amine composition and temperature range using pseudo equilibrium constant based models as used by Kent & Eisenberg.

2.9.2 Rigorous Thermodynamic Models

During the recent years, a new generation of rigorous equilibrium models have been developed which is based on the theory of strong electrolyte solutions. The historically most important *GE*-models developed for electrolyte systems can basically be divided in two groups. These are those based upon direct extensions of the Debye-Hückel limiting law for weak electrolytes and those arising from a combination of a long range term derived from Debye-Hückel theory with a short

range term arising from local composition models originally developed for molecular systems (i.e the Wilson, UNIQUAC and NRTL models).

The first significant advance in calculating activity coefficients in electrolyte solutions was achieved by Debye-Hückel (1923). The Debye-Hückel equation is based on fundamental equations of electrostatics and thermodynamics. Guggenheim (1935) was one of the first to propose a model, based on the combination of an extended Debye-Hückel equation to account for long-range ion-ion interactions, with a second order virial expansion term, to account for various short-range forces between ions of opposite charges. In a series of papers, Pitzer (1973, 1977 and 1980) proposed an excess Gibbs energy model that is based on a reformulation and extension of Guggenheim's equation. Pitzer included a third order virial term to account for short-range ternary interactions, and he allowed for short-range like ion interactions. Edwards *et al.* (1975) developed a molecular thermodynamic framework to calculate vapor-liquid equilibrium composition for a dilute aqueous system containing weak electrolytes, such as CO_2 and NH_3 . The activity coefficients were calculated using an extended Guggenheim equation (Guggenheim, 1935). Cruz and Renon (1978) developed a new function for the excess Gibbs energy of a binary electrolyte solution (single electrolyte in water) by combining the thermodynamic concepts of both Debye-Hückel theory and non-electrolyte local composition theory (NRTL equation) proposed by Renon and Prausnitz (1968). The model by Desmukh and Mather (1981) is based upon the Guggenheim equation for all activity coefficients except water. The temperature dependence of the alkanolamine protonation and the carbamate reversion were treated as adjustable parameters and the model was able to represent VLE-data for MEA- CO_2 - H_2O to ionic strengths approaching 5 mol/litre. Chen *et al.*, (1982) and Chen and Evans (1986) proposed that the excess Gibbs energy of an electrolyte solution could be written as the sum of contributions from long-range ion-ion electrostatic interactions and from short-range interactions between all true species: ion-ion, ion-molecule, and molecule-molecule. Austgen *et al.* (1989) proposed a thermodynamically rigorous model based on the electrolyte-NRTL model of

Chen and Evans (1986). To model the limiting case of amine-water, Austgen (1989) found as much total pressure data from the literature as he could and regressed it. Unfortunately activity coefficients for amine and water are not very sensitive to total pressure data at industrially important conditions. Chang (1992) improved amine-water modeling by measuring and regressing binary freezing point depression data. However the enthalpy predictions of his amine-water models were still not correct. Posey (1996) contributed towards the more accurate temperature dependence of the model by measuring excess enthalpy for MEA, DEA, MDEA solutions. Posey (1996) also improved the prediction ability of the model for very low acid gas loaded solutions, by performing conductivity and pH measurements of the low acid gas loaded solutions to predict the hydroxide ion concentration and acid gas loading up to a temperature limit of 50 and 40 °C, respectively although collecting accurate pH data is difficult due to the loss of the absorbed gases, specially for amine-CO₂ systems. pH might not be a good measure of loading in an industrial process stream where significant amount of salts or other contaminants affect the measured pH. Conductivity data are not reliable for concentrated amine solutions and above a CO₂ loading of 0.0001. Austgen's (1989) implementation of electrolyte-NRTL model in acid gas-alkanamine system is one of the sophisticated models in the recent times, but it is somewhat more complex and is certainly more expensive computationally (Weiland *et al.*, 1993). It is important that any proposed VLE model should meet the requirement of thermodynamic soundness and broad generality at a computationally affordable price.

Weiland *et al.* (1993) provided values for the interaction parameters of the Deshmukh Mather model for most of the commercially important amine systems and implemented this in the commercial code ProTreat (Optimized Gas Treating, Inc.). The Pitzer model has recently been applied for the solubility and speciation modeling of aqueous systems of CO₂ and alkanolamines (Li and Mather, 1994; Silkenbäumer *et al.*, 1998; Kamps *et al.*, 2001).

Kaewschian *et al.* (2001) used electrolyte- UNIQUAC model (Sander *et al.*, 1986) to predict the solubility of CO₂ and H₂S in aqueous solution of MEA

and MDEA. They adopted the concept of interaction between ion-pairs instead of between individual ions. This resulted in a simplification of the activity coefficient expressions compared to electrolyte-NRTL model, and required fewer interaction parameters.

Chapter 3

APPROXIMATE THERMODYNAMIC MODELING

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APPROXIMATE THERMODYNAMIC MODELING

3.1 INTRODUCTION

For the rational design of the gas treating processes, the equilibrium solubility of acid gases over alkanolamines are essential. The solubility data at very low acid gas loading and very high CO₂ partial pressures are scarcely available and that too of poor precision. It is essential to correlate the available data with a thermodynamic framework, which can be extrapolated confidently to predict the solubility data of that region. The first approach to correlate the solubility data for a CO₂/alkanolamine/water system was made by Mason and Dodge (1936). However, it was only a curve-fitting approach, and the reactions between alkanolamines and CO₂ had not been studied. Danckwerts and McNeil (1967) used pseudo equilibrium constants which did not contain activity coefficients and related these constants to the ionic strength of the solution. Kent and Eisenberg (1976) developed a simple model for predicting equilibrium solubility of acid gases over alkanolamine solvents neglecting activity

coefficients. Their model is based on several equilibrium constants and the Henry's law relationship. A more rigorous and sophisticated model was suggested by Deshmukh and Mather (1981). Their model explicitly accounts for activity coefficients and all of the possible ionic and molecular species. However, it is complex and requires solution of a set of nonlinear equations, with a certain degree of computational rigour. The equilibrium model proposed in this chapter is based on the Kent and Eisenberg approach for CO₂/alkanolamine/water systems without a serious computational burden and without compromising the accuracy of correlation and prediction capability of the developed model.

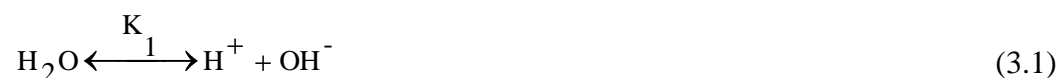
3.2 DEVELOPMENT OF APPROXIMATE THERMODYNAMIC MODEL FOR THE VAPOUR – LIQUID EQUILIBRIUM OF CO₂ INTO SINGLE ALKANOLAMINE SOLUTIONS

3.2.1 Chemical Equilibria

The CO₂ from the gas phase that dissolve into the liquid react partially with the amines to produce a number of ionic species. Ionic species are treated as nonvolatile and the vapor pressures of amines are assumed negligible in the temperature range under consideration.

In the aqueous phase for the (CO₂ – alkanolamine – H₂O) systems like (CO₂ – MEA – H₂O) & (CO₂ – DEA – H₂O) the following chemical equilibria are involved

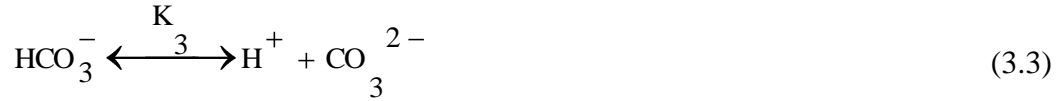
Ionization of water



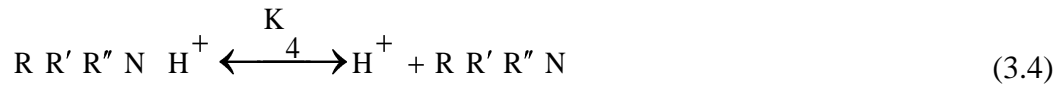
Hydration of carbon dioxide



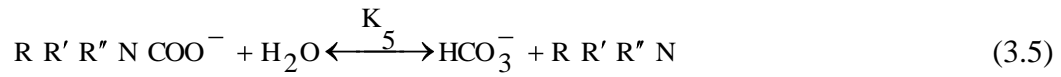
Dissociation of bicarbonate



Dissociation of protonated amine



Dissociation of carbamate



For MEA, R, R' and R'' represent H, H, and C₂H₄OH respectively; for DEA, R, R' and R'' are H, C₂H₄OH, and C₂H₄OH respectively.

From these reactions, the following equilibrium relations can be written as

$$K_1 = [\text{H}^+][\text{OH}^-] \quad (3.6)$$

$$K_2 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (3.7)$$

$$K_3 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (3.8)$$

$$K_4 = \frac{[H^+][R' R'' N]}{[R' R'' N H^+]} \quad (3.9)$$

$$K_5 = \frac{[HCO_3^-][R' R'' N]}{[R' R'' N COO^-]} \quad (3.10)$$

The following balance equations for the reacting species can be formed:

Total amine balance:

$$m = [R' R'' N] + [R' R'' N H^+] + [R' R'' N COO^-] \quad (3.11)$$

Carbon dioxide balance:

$$m\alpha = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [R' R'' N COO^-] \quad (3.12)$$

Equation of electroneutrality:

$$[H^+] + [R' R'' N H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [R' R'' N COO^-] \quad (3.13)$$

3.2.2 Vapour-Liquid Equilibria

In the low to moderate range of CO₂ partial pressure, the fugacity of CO₂ is assumed to be its partial pressure and solubility of CO₂ is identical to Henry's constant (H_{CO_2}). The vapour pressure of CO₂ is related to the free acid gas concentration in the liquid through Henry's law. The vapour-liquid equilibrium of

CO₂ over the aqueous alkanolamine solvent, assuming no solvent species in the vapour phase, is given as follows,

$$p_{\text{CO}_2} = H_{\text{CO}_2} [\text{CO}_2] \quad (3.14)$$

3.2.3 Thermodynamic Framework

In (CO₂ – alkanolamine - H₂O) system, neutral species – pure alkanolamine (DEA or MEA) and H₂O, and ionic species - protonated Alkanolamine, HCO₃⁻ and carbamate ion (DEACOO⁻ or MEACOO⁻) in the equilibrated liquid phase have been considered.

After simplification, equations (3.12) & (3.13) will be

$$m\alpha = [\text{HCO}_3^-] + [\text{R R' R'' N COO}^-] \quad (3.15)$$

$$[\text{R R' R'' N H}^+] = [\text{HCO}_3^-] + [\text{R R' R'' N COO}^-] \quad (3.16)$$

Comparing equation (3.15) & (3.16), we will have

$$m\alpha = [\text{R R' R'' N H}^+] \quad (3.17)$$

Putting the value of $[R R' R'' N]$ & $[HCO_3^-]$ from equation (3.11) & (3.15) respectively into equation (3.10) and after rearranging, we get

Putting the value of $[R R' R'' N H^+]$ from equation (3.17) into equation (3.18), we get

After rearranging the equation (3.19) will be

After solving, we will have

Putting the value of $[R R' R'' N COO^-]$ into equation (3.11) & (3.16), we get

$$[R R' R'' N] = m - m\alpha - z \quad (3.22)$$

$$[HCO_3^-] = m\alpha - z \quad (3.23)$$

Where,

$$z = \frac{\left(\left(\frac{K_4}{K_2} + m \right) \left[\left(\frac{K_4}{K_2} + m \right)^2 - 4m^2\alpha \right] - \alpha \right)^{\frac{1}{2}}}{2}$$

Putting the value of $[H^+]$ & $[HCO_3^-]$ from equation (3.9) & (3.10) into equation (3.7) and we get,

3.2.4 Thermodynamic Expression of Equilibrium Partial Pressure

Substitute this value $[CO_2]$ and putting the values of $[R'R''NH^+]$, $[R'R''NCOO^-]$ and $[R'R''N]$ from (3.17), (3.21) and (3.22) into equation (3.14) and the equation will be

$$P_{CO_2} = H_{CO_2} \frac{K_4 K_5}{K_2} \frac{m\alpha z}{\left(\left(\frac{K_4}{K_2} + m \right) \left[\left(\frac{K_4}{K_2} + m \right)^2 - 4m^2\alpha \right] - \alpha \right)^{\frac{1}{2}}} \quad (3.25)$$

Where,

$$z = \frac{\left(\left(\frac{K_4}{K_2} + m \right) \left[\left(\frac{K_4}{K_2} + m \right)^2 - 4m^2\alpha \right] - \alpha \right)^{\frac{1}{2}}}{2}$$

3.3 DEVELOPMENT OF APPROXIMATE THERMODYNAMIC MODEL FOR THE VAPOUR – LIQUID EQUILIBRIUM OF CO₂ INTO BLENDED ALKANOLAMINE SOLUTIONS

The use of mixed amine solvents in gas treating processes is of increasing interest today. A mixed amine solvent, which is an aqueous blend of a primary or secondary amine with a tertiary amine or a hindered amine, combines the higher equilibrium capacity of the tertiary amine/ hindered amine with the higher reaction rate of the primary or secondary amine that can bring about considerable improvement in gas absorption and great savings in regeneration energy requirements. Blended amine solvents are less corrosive, and require lower circulation rates to achieve the desired degree of sweetening. Because of the need to exploit poorer quality crude and natural gas coupled with increasingly strict environmental regulations, highly economical and selective acid treating processes are more important now a days. As a result, there has been a resurgence of interest in improved alkanolamine solvents and particularly in aqueous blends of alkanolamines. A simulation study with blends of (MDEA + MEA) has indicated considerable improvements in absorption compared with the single amine systems (Chakravarty *et al.*, 1985; Katti and Wolcott, 1987). The realization of such benefits in practice is a function of proper equipment design, which requires the knowledge of equilibrium solubility of the acid gases in amine blends.

The following chemical equilibria are involved in the aqueous phase for the (CO₂ – MEA – MDEA-H₂O) system

Ionization of water



Hydration of carbon dioxide



Dissociation of bicarbonate



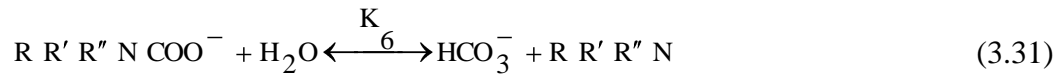
Dissociation of protonated primary amine



Dissociation of protonated tertiary amine



Dissociation of carbamate



For MEA, R, R' and R'' represent H, H, and C₂H₄OH respectively; for MDEA, R and R' are CH₃ and C₂H₄OH respectively.

From these reactions, the following equilibrium relations can be written as

$$K_1 = [\text{H}^+][\text{OH}^-] \quad (3.32)$$

$$K_2 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (3.33)$$

$$K_3 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (3.34)$$

$$K_4 = \frac{[H^+][R R' R'' N]}{[R R' R'' N H^+]} \quad (3.35)$$

$$K_5 = \frac{[H^+][R R' R' N]}{[R R' R' N H^+]} \quad (3.36)$$

$$K_6 = \frac{[HCO_3^-][R R' R'' N]}{[R R' R'' N COO^-]} \quad (3.37)$$

The following balance equations for the reacting species can be formed:

Total amine balance:

$$m_1 = [R R' R'' N] + [R R' R'' N H^+] + [R R' R'' N COO^-] \quad (3.38)$$

$$m_2 = [R R' R' N] + [R R' R' N H^+] \quad (3.39)$$

Carbon dioxide balance:

$$m_1 + m_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [R R' R'' N COO^-] \quad (3.40)$$

Equation of electro neutrality

$$[H^+] + [R R' R'' N H^+] + [R R' R' N H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [R R' R'' N COO^-] \quad (3.41)$$

The CO₂ equilibrium partial pressure is related to the physically dissolved CO₂ concentration in the aqueous blend of alkanolamine by Henry's law

$$p_{CO_2} = H_{CO_2} [CO_2] \quad (3.42)$$

For the (CO₂ – MEA - MDEA - H₂O) system, the equilibrated liquid phase is assumed to contain three molecular species (H₂O, MEA, and MDEA) and four ionic species (MDEAH⁺, HCO₃⁻, MEAH⁺, and MEACOO⁻). In this system for CO₂ loading below 1.0 does not result in significant error in the VLE predictions.

After simplification, from equation (3.40) and (3.41), we get

Solving equation (3.43) and (3.44), we get

$$m_1 \alpha = [R R' R'' N H^+] \quad (3.45)$$

$$m_2 \alpha = [R R' R' N H^+] \quad (3.46)$$

Equation (3.21) can be written as

After simplification

$$[R \ R' \ R'' \ N] = m_1 - m_1 \alpha - z \quad (3.48)$$

$$[R \ R' \ R' \ N] = m_2 - m_2 \alpha \quad (3.49)$$

Putting the value of $[H^+]$ & $[HCO_3^-]$ from equation (3.35), (3.36) & (3.37) into equation (3.33) and we get,

3.3.1 Thermodynamic Expression of Equilibrium Partial Pressure

From equations (3.32)- (3.50) we get the expression of partial pressure of CO_2 over aqueous MEA / MDEA solutions as follows,

$$p_{CO_2} = H_{CO_2} \left(\frac{K_4 m_1 \alpha}{m_1 - m_1 \alpha - z} + \frac{K_5 m_2 \alpha}{m_2 - m_2 \alpha} \right) \frac{K_6 z}{K_2 (m_1 - m_1 \alpha - z)} \quad (3.51)$$

Where,

simple case this might be the minimization or maximization of some system characteristic that is dependent on x . In a more advanced formulation the objective function, $f(\mathbf{x})$, to be minimized or maximized, might be subject to constraints in the form of equality constraints $G_i(\mathbf{x}) = 0$, $(i=1, \dots, m_e)$ and inequality constraints; $G_i(\mathbf{x}) \leq 0$, $(i=m_e+1, \dots, m)$ and /or parameter bounds; x_l, x_u . l and u indicates lower and upper bound respectively.

A General Problem (GP) description is stated as

$$\min_x \text{imize } f(\mathbf{x}) \quad (3.52)$$

Subjected to

$$\begin{aligned} G_i(\mathbf{x}) &= 0 \quad (i=1, \dots, m_e) \\ G_i(\mathbf{x}) &\leq 0, \quad (i=m_e+1, \dots, m) \end{aligned}$$

where x is the vector of length n design parameters, $f(\mathbf{x})$ is the objective function, which returns a scalar value, and the vector function $G(\mathbf{x})$ returns a vector of length m containing the values of the equality and inequality constraints evaluated at x . An efficient and accurate solution to this problem depends not only on the size of the problem in terms of the number of constraints and design variables but also on characteristics of the objective function and constraints. When both the objective function and the constraints are linear functions of the design variable, the problem is known as a Linear Programming (LP) problem. Quadratic Programming (QP) concerns the minimization or maximization of a quadratic objective function that is linearly constrained. For both the LP and QP problems, reliable solution procedures are readily available. More difficult to solve is the Nonlinear Programming (NP) problem in which the objective function and constraints can be nonlinear functions of the design variables. A solution of the NP problem generally requires an iterative procedure

to establish a direction of search at each major iteration. This is usually achieved by the solution of an LP, a QP, or an unconstrained sub problem.

3.4.3 Unconstrained Multi-variable Optimization Techniques

Although a wide spectrum of methods exists for unconstrained optimization, methods can be broadly categorized in terms of the derivative information that is, being used or not and

Direct search: Search methods that uses only function values not the information on derivatives and are most suitable for problems that are very nonlinear or have a number of discontinuities. Some of them are as follows,

- Hooke-Jeeves' pattern search
- Nelder-Mead's sequential simplex method
- Powell's conjugate directions method
- Various evolutionary techniques

Gradient-based methods: Information on derivatives is used and is generally more efficient when the function to be minimized is continuous in its first derivative. Gradient methods use information about the slope of the function to dictate a direction of search where the minimum is thought to lie. The simplest of these is the method of steepest descent in which a search is performed in a direction, $-\Delta f$, where Δf is the gradient of the objective function. The two such methods are as follows

- Steepest Descent
- Fletcher-Reeves' Conjugate Gradient method

Second order methods: Higher order methods, such as Newton's method, are only really suitable when the second order information is readily and easily calculated,

because calculation of second order information, using numerical differentiation, is computationally expensive.

- Newton's Method
- Quasi-Newton Method (constructs an approximation of the matrix of second derivatives)

3.4.4 Optimization with the Quasi-Newton Method

Of the methods that use gradient information, the most favored are the quasi-Newton methods. These methods build up curvature information at each iteration to formulate a quadratic model problem of the form

$$\min_x \frac{1}{2} x^T H x + c^T x + b \quad (3.53)$$

where the Hessian matrix, H , is a positive definite symmetric matrix, c is a constant vector, and b is a constant. The optimal solution for this problem occurs when the partial derivatives of x go to zero, i.e.,

$$\Delta f(x^*) = Hx^* + c = 0 \quad (3.54)$$

The optimal solution point, x^* can be written as

$$x^* = -H^{-1}c \quad (3.55)$$

Newton-type methods (as opposed to quasi-Newton methods) calculate H directly and proceed in a direction of descent to locate the minimum after a number of iterations. Calculating H numerically involves a large amount of computation. Quasi-Newton methods avoid this by using the observed behavior of $f(x)$ and $\Delta f(x)$ to build up curvature information to make an approximation to H using appropriate updating techniques like BFGS.

The formula given by BFGS is

$$H_{k+1} = H_k + \frac{q_k q_k^T}{q_k^T s_k} - \frac{H_k^T s_k s_k^T H_k}{s_k^T s_k H_k} \quad (3.56)$$

Where,

$$s_k = x_{k+1} - x_k$$

$$q_k = \Delta f(x_{k+1}) - \Delta f(x_k)$$

As a starting point, H_0 can be set to any symmetric positive definite matrix, for example, the identity matrix I . The gradient information is either supplied through analytically calculated gradients, or derived by partial derivatives using a numerical differentiation method via finite differences. This involves perturbing each of the design variables, x , in turn and calculating the rate of change in the objective function. At each major iteration, k , a line search is performed in the direction

$$d = -H_k^{-1} \Delta f(x_k) \quad (3.57)$$

3.4.5 Constrained Optimization

In constrained optimization, the general aim is to transform the problem into an easier subproblem that can then be solved and used as the basis of an iterative process. A characteristic of a large class of early methods is the translation of the constrained problem to a basic unconstrained problem by using a *penalty function* for constraints that are near or beyond the constraint boundary. In this way the constrained problem is solved using a sequence of parameterized unconstrained optimizations, which in the limit (of the sequence) converge to the constrained problem. These methods are now considered relatively inefficient and have been replaced by methods that have focused on the solution of the *Kuhn-Tucker* (KT) equations. The KT equations are necessary conditions for

optimality for a constrained optimization problem. Referring to the equation (3.52), the Kuhn-Tucker equations can be stated as

$$\Delta f(\mathbf{x}^*) + \sum_{i=1}^m \lambda_i^* \Delta G_i(\mathbf{x}^*) = 0 \quad (3.58)$$

$$\lambda_i^* \Delta G_i(\mathbf{x}^*) = 0 \quad i = 1, \dots, m \quad (3.59)$$

$$\lambda_i^* \geq 0 \quad i = m_e + 1, \dots, m$$

In addition to the original constraints in equation (3.52).

The first equation describes a canceling of the gradients between the objective function and the active constraints at the solution point. For the gradients to be canceled, Lagrange multipliers (λ_i , $i = 1, \dots, m$) are necessary to balance the deviations in magnitude of the objective function and constraint gradients. Because only active constraints are included in this canceling operation, constraints that are not active must not be included in this operation and so are given Lagrange multipliers equal to zero. This is stated implicitly in the last two equations The solution of the KT equations forms the basis to many nonlinear programming algorithms. These algorithms attempt to compute the Lagrange multipliers directly. Constrained quasi-Newton methods guarantee superlinear convergence by accumulating second order information regarding the KT equations using a quasi-Newton updating procedure. These methods are commonly referred to as Sequential Quadratic Programming (SQP) methods.

3.5 FORMULATION OF OBJECTIVE FUNCTION AND METHOD OF SOLUTION

For the (CO₂ – MEA - H₂O), (CO₂ –DEA - H₂O) and (CO₂ – MEA – MDEA-H₂O) systems, the numerical values for equilibrium constants, namely deprotonation constant and carbamate reversion constant were determined by

optimizing the objective function, which, in general, is the difference between the measured values of equilibrium CO₂ partial pressures and the values calculated from the developed model. However, simple minimization of the sum of differences between measured and calculated values would weigh the high partial pressure data almost to the exclusion of the low partial pressure data. Hence, the objective function used in this work is the sum of the individual discrepancy functions:

$$F = \sum (p_i^{\text{exp}} - p_i^{\text{cal}})^2 \quad (3.60)$$

The MATLAB 7.6 optimization toolbox has been used extensively for the present work. '*fmincon*' function, which is a constrained optimization function using quasi-Newton and Sequential Quadratic Programming (SQP) methods, have been used here for minimization of the proposed objective functions with variable bounds. The functions like '*lsqcurvefit*' and '*lsqnonlin*' also have been tried to achieve best possible prediction of CO₂ partial pressure over the alkanolamine solutions. For the presently formulated phase equilibrium problem the performance of '*fmincon*' proved to be comparatively better than other functions. The converged solutions obtained were initial guess independent.

3.6 RESULTS AND DISCUSSIONS

3.6.1 Determination of Equilibrium Constants for Single Alkanolamine System

The free CO₂ concentration in the liquid phase can be calculated through the computational techniques. In this work, literature values (Li and shen, 1993) of all equilibrium constants except K₄ and K₅ and Henry's constant were used and are summarized in Table 3.1. The amine deprotonation constant K₄ and

carbamate stability constant K_5 were determined by forcing a fit with the experimental solubility data. To solve this system of nonlinear algebraic equation, initial estimates of the concentrations had to be provided and the quasi-Newton method was used. In all cases, false convergence had not arisen.

For the (CO_2 – MEA - H_2O) system, the deprotonation constants (K_4) and the carbamate stability constants (K_5) were determined regressing the solubility of CO_2 in 30 wt % aqueous MEA solutions at 40, 60, 80 and 100 °C. The literature data has been taken from Shen and Li (1993) and model equation (3.25) was used. The average absolute percentage deviations between the experimental and model correlated CO_2 partial pressure (%AAD correlation) ranges from 12.9 -19.2 and they are listed in Table 3.2. The model predictions are in good agreement with the literature data over a wide temperature, amine composition and CO_2 partial pressure as depicted in Table 3.5. The prediction results of the (CO_2 -MEA- H_2O) system are shown in Figures 3.1, 3.2, 3.3 and 3.4. Figure 3.5, is a parity plot showing a comparison of the predicted results with the experimental results for the (CO_2 -MEA- H_2O) system.

For the (CO_2 – DEA - H_2O) system, the model equation (3.25) was used to determine the deprotonation constants (K_4) and the carbamate stability constants (K_5). The different literature values used for correlation are presented in Table 3.3. The correlation results are in good agreement with the experimental data with an average absolute percentage deviations of correlation (difference between the experimental and model correlated CO_2 partial pressure) ranging from 4.77- 23.6 and are listed in Table 3.3. The model predictions are in reasonable agreement with data available in the open literature and are listed in Table 3.6. The prediction results of the (CO_2 -DEA- H_2O) system are shown in Figures 3.6 and 3.7.

3.6.2 Determination of Equilibrium Constants for Blended Alkanolamine System

For the (CO_2 – MEA - MDEA - H_2O) system, the model equation (3.51) was used to determine the deprotonation constants (K_5) of MDEA. In this work, literature values (Li and shen, 1993) of all equilibrium constants (K_1 , K_2 and K_3) and Henry's constant were used. These are summarized in Table 3.1. The deprotonation constants (K_4) and the carbamate stability constants (K_6) of MEA were used from our previously regressed values for the (CO_2 – MEA - H_2O) system. The deprotonation constant of MDEA (K_5) was determined from the solubility of CO_2 in 12 wt % MEA + 18 wt% MDEA aqueous solutions at 40, 60, 80 and 100 °C from data available in Shen and Li (1993). The average absolute percentage deviations of correlation (difference between the experimental and model correlated CO_2 partial pressure) ranges from 18.12- 31 and are listed in Table 3.4. The model predictions are in reasonable agreement with data available in the open literature and are listed in Table 3.7.

3.7 CONCLUSION

The Kent and Eisenberg approach has been extended to represent the solubility of CO_2 in aqueous mixtures of single and blended alkanolamine solutions. The literature values for ionization constants and Henry's law constant are adopted directly in the calculation. The deprotonation and carbamate reversion constants have been determined by regressing the solubility data of (CO_2 – MEA - H_2O), (CO_2 –DEA - H_2O) and (CO_2 – MEA - MDEA - H_2O) systems over a wide range of temperature, amine composition and CO_2 partial pressure. The accurate determination of the species like carbamate ion in the equilibrated liquid phase over the entire CO_2 loading range (below 1.0) has been the strength of the presently developed model as is evidenced by its comparatively better prediction capability compared to any previously developed

approximate model following the Kent and Eisenberg approach. For the aforesaid systems, the correlated and predicted CO₂ partial pressures by the developed model are, in general, in excellent agreement with the data available in the open literature. The model developed here for a CO₂ - aqueous primary /secondary alkanolamine/ alkanolamine blend can be confidently used for predicting VLE of CO₂ over other newly proposed alkanolamine solvents and its blends. Within a thermodynamic framework and without a serious computational burden, the proposed models have shown excellent prediction ability.

Table 3.1 Temperature dependence of the equilibrium constants and Henry's constant.

$$K_i = \exp(C_1 + C_2/T + C_3/T^2 + C_4/T^3 + C_5/T^4)$$

$$H_{\text{CO}_2} = \exp(C_1 + C_2/T + C_3/T^2 + C_4/T^3 + C_5/T^4)$$

Reaction	Equilibrium constant	C_1	$C_2 \times 10^{-4}$	$C_3 \times 10^{-8}$	$C_4 \times 10^{-11}$	$C_5 \times 10^{-13}$	Ref
3.1, 3.26	K_1	39.5554	-9.879	0.568827	-0.146451	0.136145	^a
3.2, 3.27	K_2	-241.828	29.8253	-1.48528	0.332647	-0.282393	^a
3.3, 3.28	K_3	-294.74	36.4385	-1.84157	0.415792	-0.354291	^a
3.14	$H_{(\text{CO}_2)}$	20.2629	-1.38306	0.06913	-0.015589	0.01200	^a

^a Li and Shen, 1993

Table 3.2 Equilibrium constants (Deprotonation constant, K_4 and Carbamate constant, K_5) for (CO_2 - MEA - H_2O) system.

Reference	MEA wt %	Temp (K)	Data points	CO_2 Partial pressure range (kPa)	K_4	K_5	^a AAD% Correlation
Shen and Li (1992)	30	313	12	2.2 - 1973	3.0998×10^{-10}	0.0409801	13.42
Shen and Li (1992)	30	333	10	1.1 - 1975	9.76784×10^{-10}	0.0588008	14.57
Shen and Li (1992)	30	353	9	4.5 - 1711	3.01831×10^{-9}	0.1008993	19.23
Shen and Li (1992)	30	373	10	2.8-1951	7.34505×10^{-9}	0.1121031	12.93

Table 3.3 Equilibrium constants (Deprotonation constant, K_4 and Carbamate constant, K_5) for (CO_2 - DEA - H_2O) system.

Reference	DEA (molarity)	Temp (K)	Data points	CO_2 Partial pressure range (kPa)	K_4	K_5	^a AAD% Correlation
Seo and Hong (1996)	2.85	313	5	8.8 - 283	1.01532×10^{-9}	0.1502884	7.18
Lee, Otto and Mather (1972)	0.5, 2.0, 3.5	323	14	2.17 – 687	1.86451×10^{-9}	0.5616503	19.15
Lawson and Grast (1976)	2.38	338	6	15 - 619	3.12334×10^{-9}	0.6461488	4.77
Lee, Otto and Mather (1972)	0.5, 2.0, 3.5	348	17	2.17 – 687	5.57932×10^{-9}	0.9185167	16.37
Lee, Otto and Mather (1972)	0.5, 2.0, 3.5	373	14	21.7-2170	1.08806×10^{-8}	1.6550068	23.68

$$^a \text{AAD\%} = \left[\sum_n \frac{|p_{\text{cal}} - p_{\text{exp}}|}{p_{\text{exp}}} \right] / n \times 100$$

Table 3.4 Equilibrium constant (Deprotonation constant) for (CO₂ - MDEA - H₂O) system.

Reference	MEA wt %	MDEA wt %	Temp (K)	Data points	CO ₂ Partial pressure range (kPa)	K _s	^a AAD% Correlation
Shen and Li (1992)	12	18	313	8	3.7 - 1421	2.33559×10^{-9}	21.59
Shen and Li (1992)	12	18	333	10	0.9 - 1623	5.10341×10^{-9}	29.34
Shen and Li (1992)	12	18	353	11	3.0 - 1998	7.42284×10^{-9}	25.93
Shen and Li (1992)	12	18	373	8	2.1 - 1934	8.40401×10^{-9}	32.47

Table 3.5 Prediction of Vapor-liquid equilibria of (CO₂ - MEA - H₂O) system.

Reference	MEA (molarity)	Temp (K)	Data points	CO ₂ Partial pressure range (kPa)	^a AAD% Prediction
Jones <i>et al</i> (1959)	2.5	313	6	0.3 – 120	24.13
Shen and Li (1992)	2.5	313	6	15.7 – 120.7	31.0
Lee, Otto and Mather (1974)	2.5	313	7	3.9- 488	19.71
Lee, Otto and Mather (1976)	2.5	313	5	3.2 - 316	18.12
Lee, Otto and Mather (1976)	1.0, 2.5, 3.75, 5.0	313	23	1 – 316	28.16
Lee, Otto and Mather (1976)	1.0, 2.5, 3.75, 5.0	333	27	0.316-316	20.60
Lee, Otto and Mather (1976)	1.0, 2.5, 3.75, 5.0	353	28	0.316-316	27.67
Lee, Otto and Mather (1976)	1.0, 2.5, 3.75, 5.0	373	32	0.1 - 316	22.19

Table 3.6 Prediction of Vapor-liquid equilibria of (CO₂ - DEA - H₂O) system.

Reference	DEA wt %	Temp (K)	Data points	CO ₂ Partial pressure range (kPa)	^a AAD% Prediction
Kundu <i>et al</i> (2005)	25	313	7	1.87 – 87.5	21.4
Kundu <i>et al</i> (2005)	30	313	7	3.0 - 94	12.58
Lawson and Grast (1976)	25	373	6	89.7 - 1697	16.90

Table 3.7 Prediction of Vapor-liquid equilibria of (CO₂ - MEA -MDEA- H₂O) system

Reference	MEA wt %	MDEA wt %	Temp (K)	Data points	CO ₂ Partial pressure range (kPa)	^a AAD% Prediction
Shen and Li (1992)	24	6	313	10	6.6 - 1649	21.67
Shen and Li (1992)	24	6	333	11	4.3 -1981	14.55
Shen and Li (1992)	24	6	353	11	2.0 - 1925	22.66
Shen and Li (1992)	24	6	373	10	4.0 - 1509	26.76

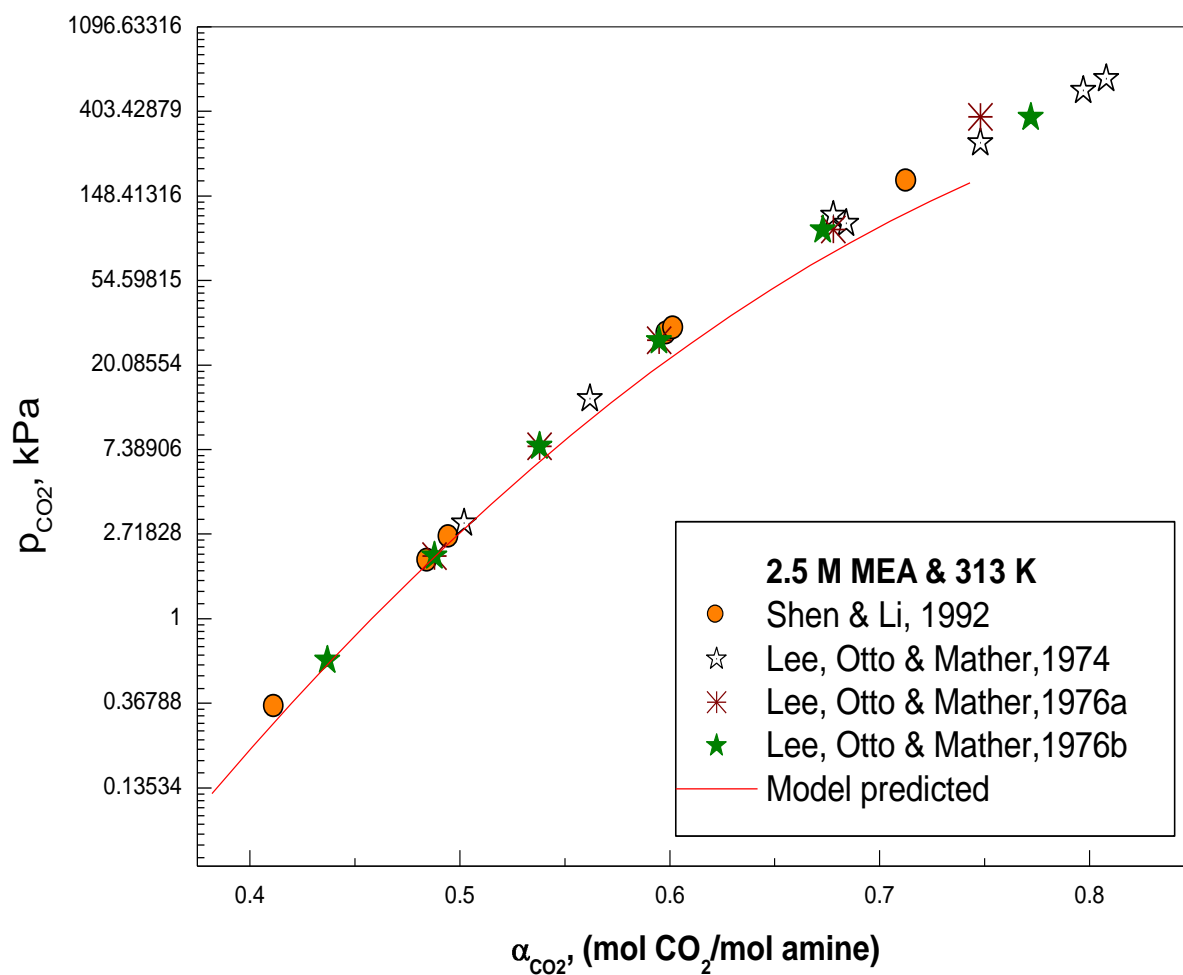


Figure 3.1 Equilibrium partial pressure of CO₂ over 2.5 M MEA solution at 313K

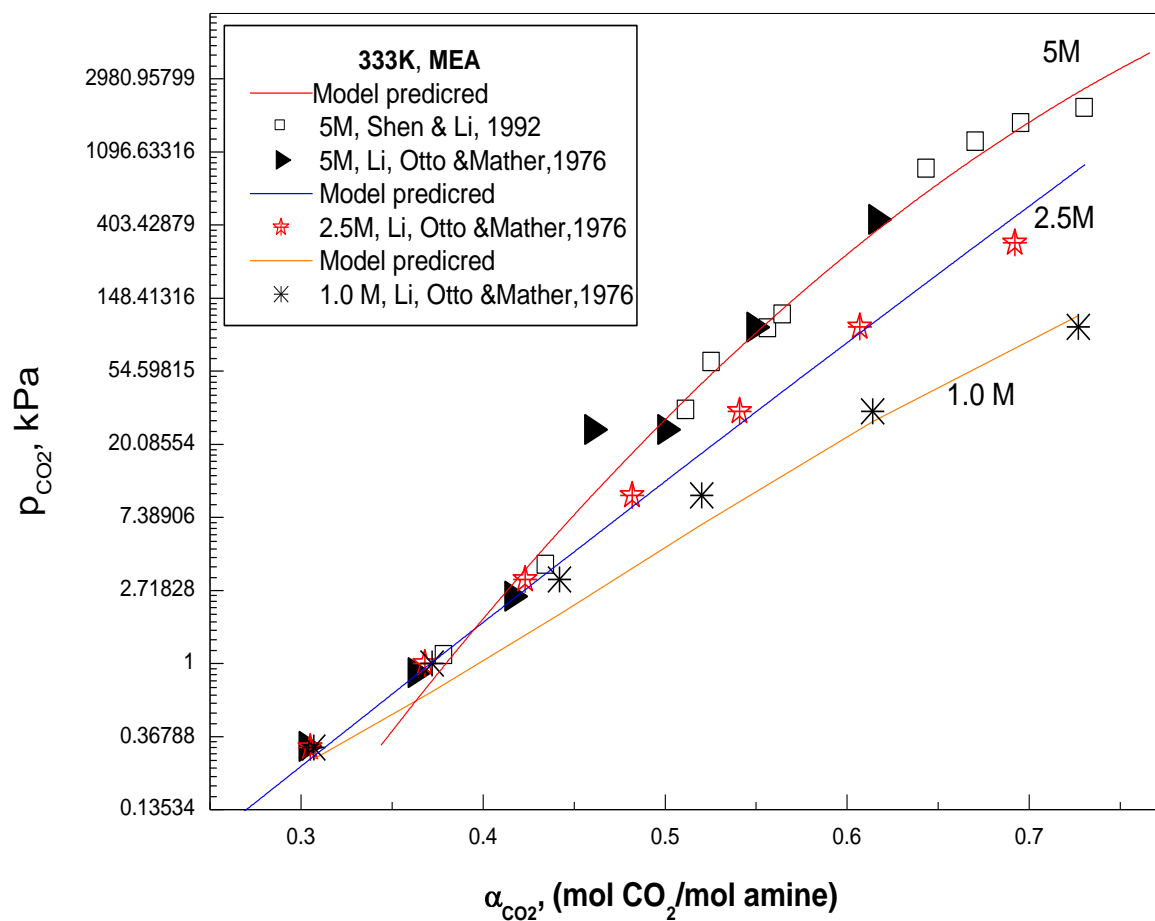


Figure 3.2 Equilibrium partial pressure of CO_2 over 5, 2.5, 1 M MEA solution at 333K

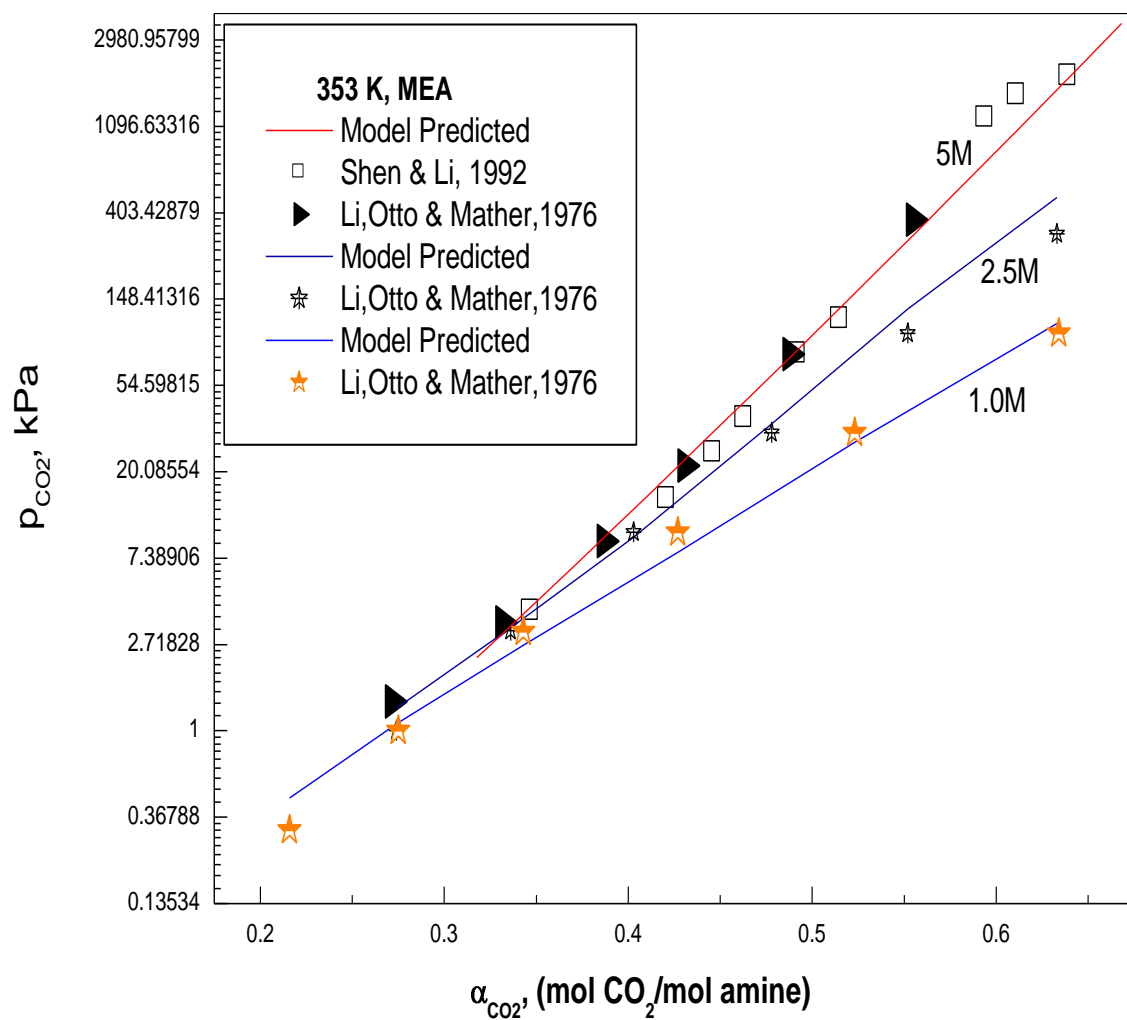


Figure 3.3 Equilibrium partial pressure of CO_2 over 5, 2.5, 1 M MEA solution at 353K

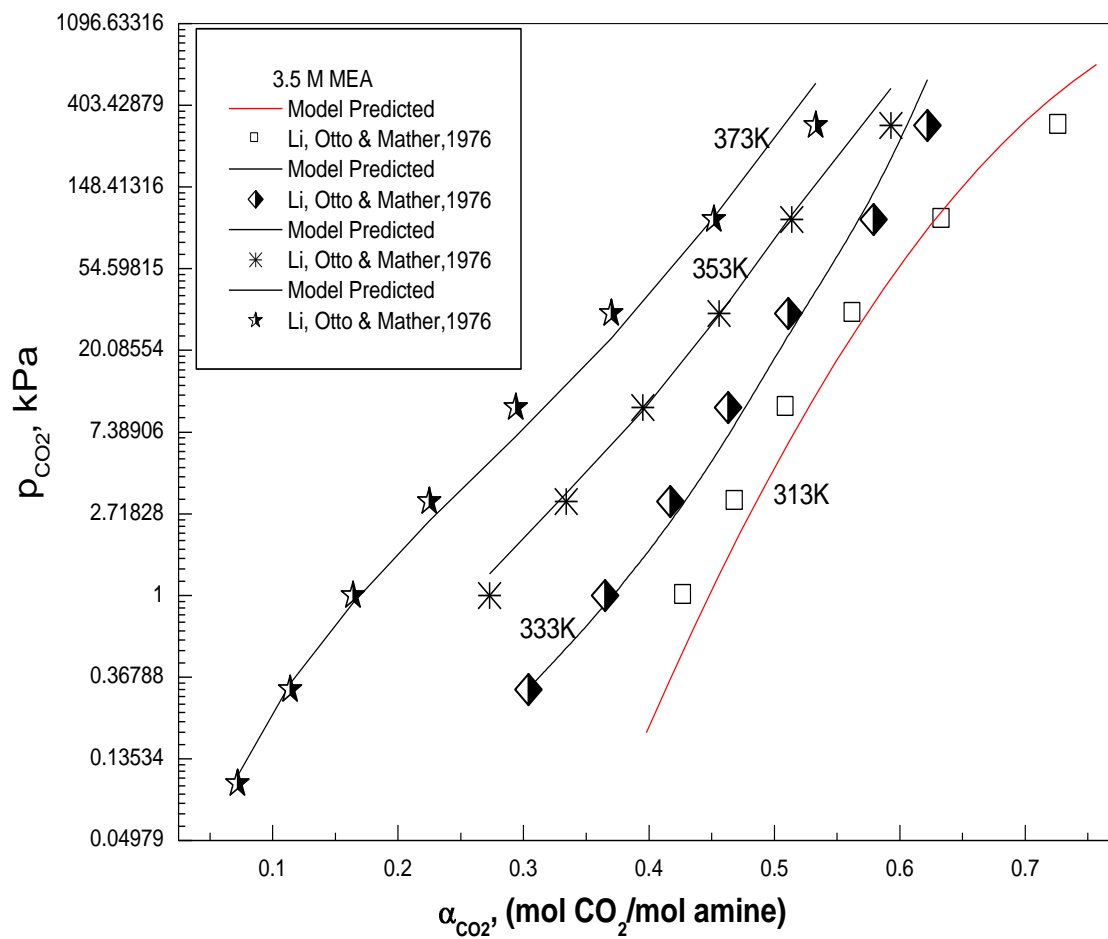


Figure 3.4 Equilibrium partial pressure of CO_2 over 3.5 M MEA solution at 313, 333, 353, 373K

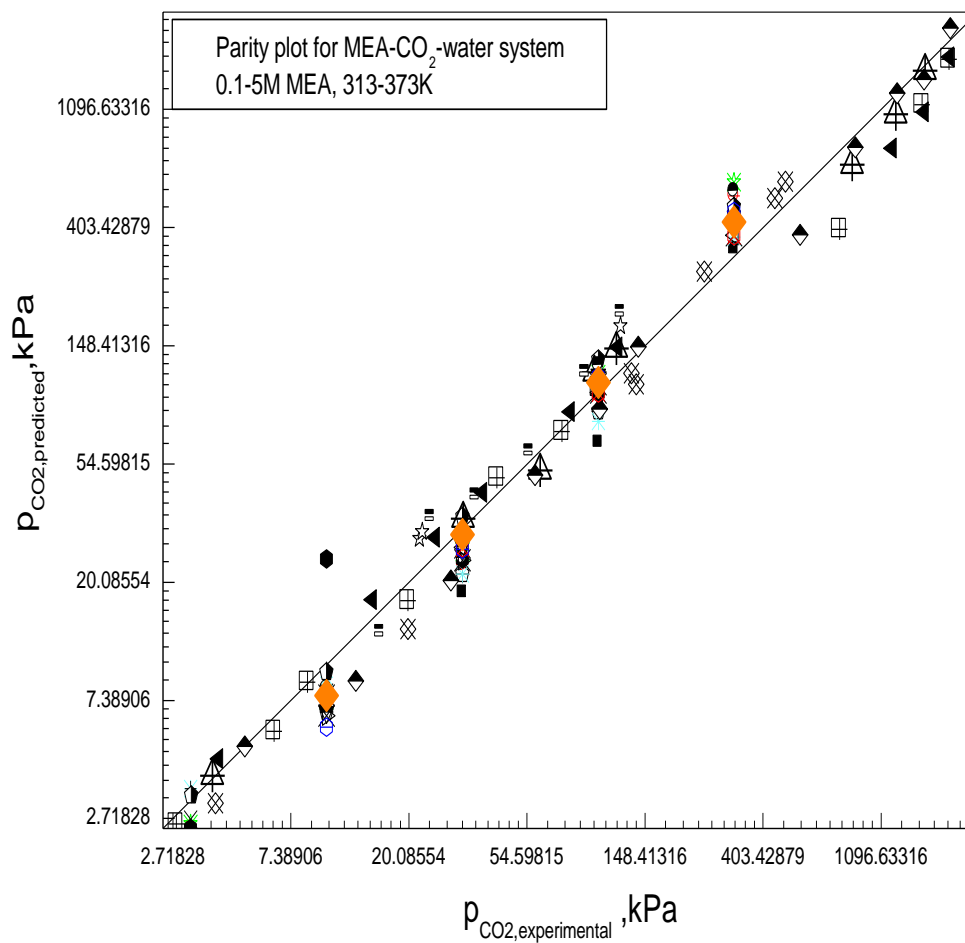


Figure 3.5 Comparison of model predicted and experimentally measured CO₂ equilibrium partial pressure over 0.1-5M MEA aqueous solutions in the temperature rang 313 -373 K.

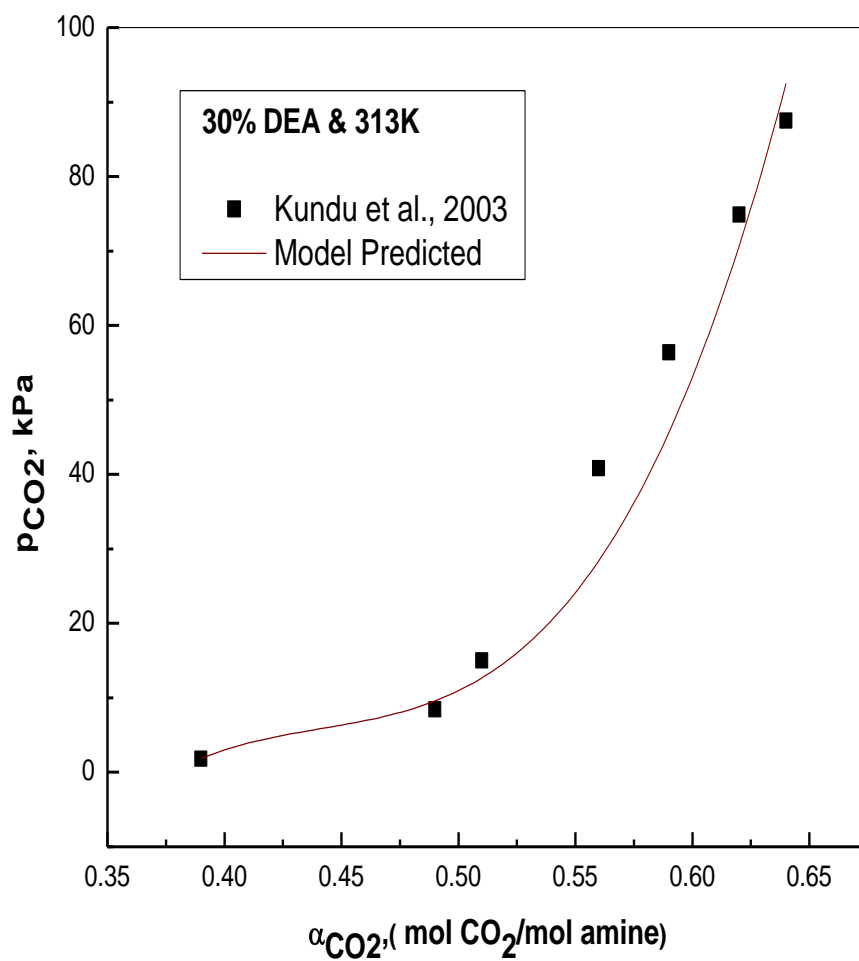


Figure 3.6 Equilibrium partial pressure of CO₂ over 30% DEA solution at 313K

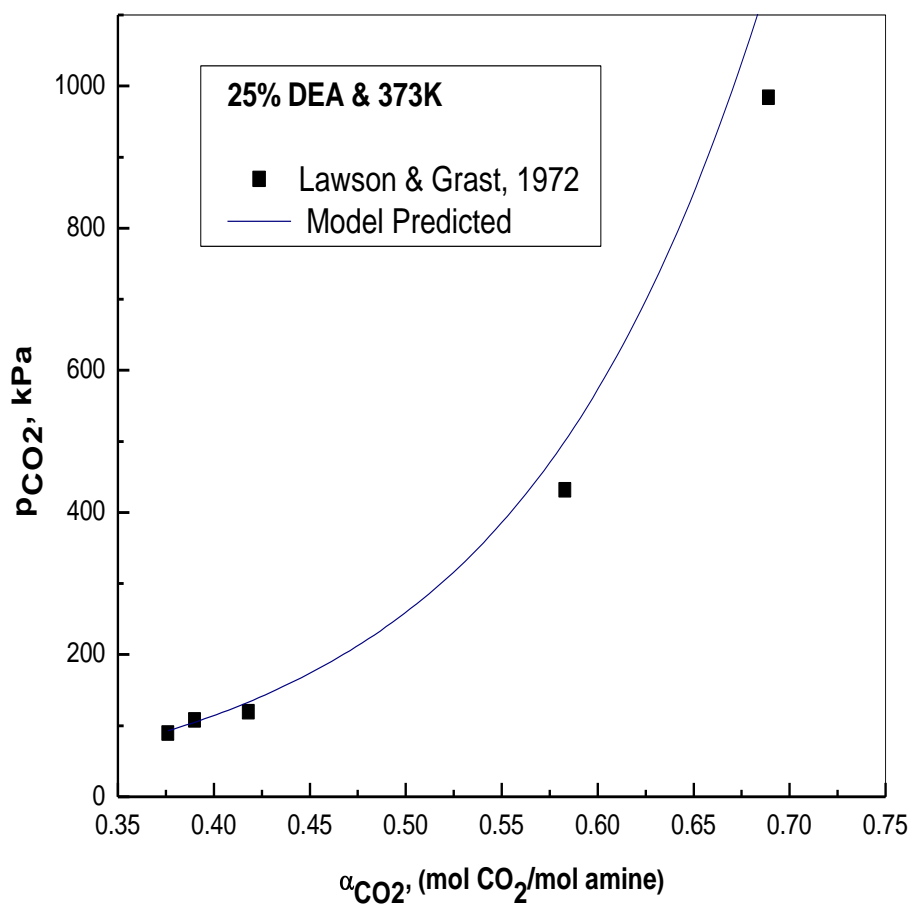


Figure 3.7 Equilibrium partial pressure of CO₂ over 25% DEA solution at 373K

Chapter 4

RIGOROUS THERMODYNAMIC MODELLING

Chapter 4

RIGOROUS THERMODYNAMIC MODELING

4.1 INTRODUCTION

Many commercial gas-treating processes are still designed by experience and heuristics resulting in over design and excessive energy consumption. The apparent thermodynamic models developed in chapter 3 merely correlated the available solubility data within a thermodynamic framework using apparent equilibrium constants, moreover some of the equilibrium constants like deprotonation and carbamate reversion constants of alkanolamines were regressed as fit parameters forcing the non-ideality to be lumped in the equilibrium constants and accurate speciation is far from impeccable. A robust thermodynamic model is required for both process design and operation of gas treating units. In this chapter, a thermodynamic model based on activity is

proposed to correlate and predict the solubility of the acid gases (H_2S and CO_2) over alkanolamine solutions. The activity based models render an insight in to the molecular physics of the system, hence accurate speciation of the equilibrated liquid phase becomes a reality besides its prediction ability of the solubility of the acid gases over alkanolamine solutions.

Deshmukh-Mather used extended Debye- Hückel theory of electrolytic solution to model the equilibria of CO_2 and H_2S over alkanolamine solution and of sufficient generality to be extremely useful. The models developed in this chapter used the approach of Deshmukh-Mather.

4.2 DEVELOPMENT OF RIGOROUS THERMODYNAMIC MODEL FOR THE VAPOUR-LIQUID EQUILIBRIUM OF CO_2 INTO AQUEOUS SINGLE ALKANOLAMINE SOLUTIONS.

Over the decades, we have witnessed some of the significant work in model development to correlate and predict the vapor-liquid equilibrium of (acid gas – aqueous alkanolamine) systems. Kent and Eisenberg (1976) created the first equilibrium model that received widespread acceptance. Their model was based on pseudo-equilibrium constants and Henry's law. They regressed the pseudo-equilibrium constants for the amine deprotonation and carbamate reversion reactions for MEA and DEA systems to fit experimental vapour-liquid equilibrium (VLE) data. This resulted in a model, which had only two parameters per acid gas to account for the ionic strength dependence of the acid gas partial pressure. The model was reasonably accurate at loadings greater than 0.1, but was inaccurate at lower loadings due to the manipulations of the amine equilibrium constants. Another drawback of this model was that it could not be used to find ionic and molecular species concentrations. By regressing the equilibrium constants they have effectively combined the activity coefficients

with species mol fractions making independent determinations of either impossible. Only (CO_2 – MEA - H_2O) and (CO_2 – DEA - H_2O) systems were studied and they reported a reasonable predictive agreement with mixed acid gas data. Atwood *et al.* (1957) proposed a method for the calculation of equilibria in the H_2S /amine/ H_2O system. The central feature of this model is the use of a “mean ionic activity coefficient”. The activity coefficients of all ionic species were assumed to be equal. This assumption is good at low ionic strengths or if only one cation and one anion are present in significant amounts. However, this is generally not the case for the $\text{CO}_2/\text{H}_2\text{S}$ /alkanolamine/ H_2O system. This model was utilized by Klyamer and Kolesnikova (1973) for the CO_2 /amine/ H_2O system and was generalized by Klyamer *et al.* (1972) to make it applicable to the $\text{CO}_2/\text{H}_2\text{S}$ /amine/ H_2O system. If the activity coefficients in the Klyamer *et al.* model are set equal to unity, the model is algebraically equivalent to the Kent and Eisenberg model. Deshmukh-Mather used extended Debye- Hückel theory of electrolytic solution to model the equilibria of CO_2 and H_2S over alkanolamine solutions. The Peng-Robinson equation of state was used to determine vapour phase fugacity coefficients. The water activity coefficient was assumed to be 1.0. The primary parameters of the model and the reaction equilibrium constants are available from independent measurements, and even by themselves, they yield a set of model predictions in fair quantitative agreement with the data. Weiland *et al.* (1993 & 1995) validated the Deshmukh Mather model with appreciable experimental VLE data of CO_2 and H_2S equilibrium in aqueous solutions of MEA, DEA and MDEA.

Present chapter proposes a rigorous thermodynamic model using extended Debye-Hückel theory of electrolytic solution with a comparatively less computational rigour than Deshmukh Mather model. The thermodynamic equilibrium is based on two types of equilibria; dissociation of electrolyte in the aqueous solution and the vapour-liquid equilibrium of the acid gas species. The fugacity coefficient, the vapor phase non-ideality correction factor has been calculated using the ‘Virial Equation of State’.

4.2.1 Equilibrium Constants

Equilibrium constants governing the dissociation of weak electrolytes in aqueous solutions are customarily reported on the molality scale with the asymmetric activity coefficient convention for all species ($\gamma_i \rightarrow 1$ as $x_i \rightarrow 0$). The temperature dependence of logarithm of equilibrium constant is often reported as

$$\ln K_i = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T \quad (4.1)$$

The coefficients C_1 through C_4 for different reactions are taken from different literature sources and presented in Table 4.1

The chemical equilibrium constants in this work should adopt the same reference states for each component in equilibrium. In the measurement of the dissociation constants of protonated alkanolamines, the amines are treated as solutes with asymmetrically normalized activity coefficients. Using this reference state the activity coefficient of alkanolamine goes to unity at infinite dilution

4.2.2 Chemical Equilibria

In the (CO_2 – alkanolamine – H_2O) systems, the following 12 species are postulated to exist in solution: CO_2 , HCO_3^- , CO_3^{2-} , R R' R'' N COO^- , R R' R'' N^+ , H_2O , H^+ , and OH^- . Here, R R' R'' N represents the amine and the R , R' and R'' groups may be mobile protons or hydrocarbon groups depending on the amine in question. In general terms, the equilibrium distribution of CO_2 in an aqueous alkanolamine solution and a vapor phase is determined by the solution of a set of equations comprising (i) two species balances, one for CO_2 ,

and the amine (S, C, and N), (ii) seven reaction equilibrium equations for the dissociation of various species in solution, (iii) an equation of electroneutrality, and (iv) isofugacity statements for each species which is present in both phases.

In the aqueous phase for the (CO₂ – alkanolamine – H₂O) systems like ((CO₂ – MEA – H₂O), & (CO₂ – DEA – H₂O)) the chemical equilibria involved are already discussed in eqs.3.1-3.5.

Mathematically, the corresponding equilibrium constants are defined in terms of activity coefficients, γ , and molalities, m of the species present in the equilibrated liquid phase.

$$K_1 = \frac{\gamma_{H^+}^m \gamma_{OH^-}^m}{\gamma_{H^+}^m \gamma_{OH^-}^m} \quad (4.2)$$

$$K_2 = \frac{\gamma_{H^+}^m \gamma_{HCO_3^-}^m}{\gamma_{CO_2}^m \gamma_{HCO_3^-}^m} \quad (4.3)$$

$$K_3 = \frac{\gamma_{H^+}^m \gamma_{CO_3^{2-}}^m}{\gamma_{HCO_3^-}^m \gamma_{HCO_3^-}^m} \quad (4.4)$$

$$K_4 = \frac{\gamma_{H^+}^m \gamma_{R'R''N}^m}{\gamma_{R'R''N}^m \gamma_{H^+}^m} \quad (4.5)$$

$$K_5 = \frac{\gamma_{\text{HCO}_3^-}^m \gamma_{\text{HCO}_3^-}^m \gamma_{\text{R R' R'' N}^m \text{R R' R'' N}}}{\gamma_{\text{R R' R'' N COO}^-}^m \gamma_{\text{R R' R'' N COO}^-}^m} \quad (4.6)$$

For MEA, R, R' and R'' represent H, H, and C₂H₄OH respectively; for DEA, R, R' and R'' are H, C₂H₄OH, and C₂H₄OH respectively.

The following balance equations for the reacting species can be formed:

Total amine balance:

$$m_t = m_{\text{R R' R'' N}} + m_{\text{R R' R'' N H}^+} + m_{\text{R R' R'' N COO}^-} \quad (4.7)$$

Carbon dioxide balance:

$$m_t \alpha = m_{\text{CO}_2} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} + m_{\text{R R' R'' N COO}^-} \quad (4.8)$$

Equation of electroneutrality:

$$m_{\text{H}^+} + m_{\text{R R' R'' N H}^+} = m_{\text{OH}^-} + m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{R R' R'' N COO}^-} \quad (4.9)$$

Here, m_t indicates total concentration of the amine in all its forms (i.e., the initial, acid-gas-free amine concentration) and α is the loading of the acid gas in question

(moles of acid gas per mole of total amine). The vapor and liquid phases are connected by isofugacity equations.

4.2.3. Vapour-Liquid Equilibria

We have assumed that the amine is nonvolatile (relative to the other molecular species), an assumption that can be easily relaxed if necessary. It is assumed a physical solubility (Henry's law) relation for the (noncondensible) acid gases and a vapor pressure relation for water. (If the system contains other volatile species, such as hydrocarbons, these can be accounted for by additional isofugacity relations based, for example, on Henry's law for sparingly soluble components, or on vapor pressures for condensibles.) Thus, the following relations apply:

$$\Phi_{\text{CO}_2} y_{\text{CO}_2} P = \gamma_{\text{CO}_2} m_{\text{CO}_2} H_{\text{CO}_2} \quad (4.10)$$

Where, Φ_{CO_2} is the fugacity coefficient of CO_2 , y_{CO_2} is mole fraction, H_{CO_2} is a Henry's constant for the acid gas in pure water, P is the total pressure. The Henry's constant are taken from literature and presented in Table 4.1. The vapor phase fugacity coefficient has been calculated using the 'Virial Equation of State'.

4.2.4 Thermodynamic Framework

In (CO_2 – alkanolamine - H_2O) system, the existence of neutral species – pure alkanolamine (DEA, MEA) and H_2O , and ionic species - protonated Alkanolamine, HCO_3^- and carbamate ion (DEACOO^- , MEACOO^-) in the equilibrated liquid phase have been considered. For simplicity, the free molecular

species CO_2 and the ionic species CO_3^{2-} and OH^- in the liquid phase have been neglected since concentration of these species are very low compared to the other species present in the equilibrated liquid phase. Several previous workers (Li and Mather, 1994, 1997; Haji-Sulaiman *et al.*, 1996; Posey, 1996) have observed that neglecting the concentrations of free molecular CO_2 , and OH^- and CO_3^{2-} ions in the liquid phase in this system for CO_2 loading below 1.0 does not result in significant error in the VLE predictions. It is thus assumed that almost all of the dissolved CO_2 is converted into HCO_3^- ions. In our calculation of activity coefficients of the components in the aqueous phase, the activity coefficients of pure alkanolamine, H_2O , protonated alkanolamine, and HCO_3^- are included to account for the non-ideality of the liquid phase. As the free molecular CO_2 concentration in the liquid phase is negligible below the loading of 1.0, the value of γ_{CO_2} will be close to unity following the asymmetric normalization of activity coefficient. We can calculate liquid phase molality based on true molecular or ionic species.

4.2.5 Activity Coefficient Model

The activity coefficient model consists of Debye-Hückel term, which is one of the dominant term in the expression for the activity coefficients in dilute solution, accounts for electrostatic, non-specific long-range interactions. At higher concentrations short range, non-electrostatic interactions have to be taken into account. This is usually done by adding ionic strength dependent terms to the Debye-Hückel expression. This method was first outlined by Brønsted, and elaborated by Scatchard and Guggenheim. The mathematical description of the two basic assumptions in the specific ion interaction theory are as follows,

$$\ln \gamma_i = -\frac{Az_i^2 I^{0.5}}{1 + I^{0.5}} + 2 \sum_j \beta_{ij} m_j \quad (4.11)$$

Here, A , is the Debye- Hückel limiting slope (0.509 at 25 °C in water), and I is the ionic strength, defined as

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (4.12)$$

Here, z_i is the charge number on the ion, β_{ij} represent the net effect of various short-range two-body forces between different molecular and ionic solutes. The summation in the second term is taken over all solute pairs but excludes interactions between solutes and the solvent, water. Physically, the first term on the right represents the contribution of electrostatic forces; the second term represents short-range van der Waals forces. This model performs reasonably well in fitting data for dilute solutions; however, for concentrated solutions of weak electrolytes (above 10 M concentration), Pitzer's correlation (Pitzer, 1973) performs better. Nevertheless, we have used the extended Debye-Hückel theory for a number of reasons: First, this is the form invariably used while obtaining the dissociation constants of various species. Second, it reduces to the well-known Setschenow (1889) equation for the salting-out effect caused by molecule-ion interactions, and third, it gives the correct limiting behavior for solutions of low ionic strength. The approach of Guggenheim and Stokes allows this to be done using only single-amine parameters; the use of Pitzer's correlation would require an unmanageably large number of additional parameters.

There are an extremely large number of possible interactions in acid-gas alkanolamine systems. For example, for a primary or secondary amine with two acid gases, there are 78 possible interactions (even allowing for symmetry). In a blended amine system in which both amines can form carbamates there are 120 possible interactions. Interactions between ions of the same charge (ie., net positive or negative) are neglected. All interactions between like-charged ions (Bronsted, 1922), all self-interactions of molecular species (with the sole exception of molecular amine with itself), and all interactions between water and

its ionization products with other species were set to zero. This still leaves 27 parameters for a two-acid-gas, carbamate-forming system. To reduce further the number of parameters to a manageable set, interactions between the acid gases and other components were disregarded for the primary and secondary amine systems; this was justified that nonzero values of the parameters were found to have negligible effect on calculated partial pressures. This is a result that one might expect on the basis of the concentrations of most of these species being quite small (so that even if their interactions were strong, they would make negligible contribution to the total interaction term. The interactions (β_{ij}) which are considered finally are as follows,

$$\begin{aligned} & \beta \left(R' R'' N COO^- - R R' R'' N H^+ \right) \\ & \beta \left(R' R'' N COO^- - R R' R'' N \right) \\ & \beta \left(R R' R'' N H^+ - HCO_3^- \right) \\ & \beta \left(R' R'' N - R R' R'' N H^+ \right) \\ & \beta \left(R R' R'' N - HCO_3^- \right) \end{aligned}$$

For MEA, R, R' and R'' represent H, H and C₂H₄OH respectively; for DEA, R, R' and R'' are H, C₂H₄OH, and C₂H₄OH respectively.

Putting the value of $\gamma_{CO_2} m_{CO_2}$ from equation (4.3) into equation (4.10) and the equation will be

$$\Phi_{CO_2} y_{CO_2} P = \frac{\gamma_{H^+} m_{H^+} \gamma_{HCO_3^-} m_{HCO_3^-}}{K_2} H_{CO_2} \quad (4.13)$$

Substitute the value of $\gamma_{H^+} m_{H^+}$ and $\gamma_{HCO_3^-} m_{HCO_3^-}$ from equation (4.5) and (4.6) into (4.13) and we will have,

$$\Phi_{\text{CO}_2} y_{\text{CO}_2} P = \frac{K_4 K_5}{K_2} \frac{\gamma_{\text{R R' R'' N H}^+} m_{\text{R R' R'' N H}^+} \gamma_{\text{R R' R'' N COO}^-} m_{\text{R R' R'' N COO}^-}}{\gamma_{\text{R R' R'' N}} m_{\text{R R' R'' N}}^2} H_{\text{CO}_2} \quad (4.14)$$

$y_{\text{CO}_2} P = p_{\text{CO}_2}$; So the above equation will be

$$p_{\text{CO}_2} = \frac{H_{\text{CO}_2}}{\Phi_{\text{CO}_2}} \frac{K_4 K_5}{K_2} \frac{\gamma_{\text{R R' R'' N H}^+} m_{\text{R R' R'' N H}^+} \gamma_{\text{R R' R'' N COO}^-} m_{\text{R R' R'' N COO}^-}}{\gamma_{\text{R R' R'' N}} m_{\text{R R' R'' N}}^2} \quad (4.15)$$

The value of $m_{\text{R R' R'' N H}^+}$, $m_{\text{R R' R'' N COO}^-}$ and $m_{\text{R R' R'' N}}$ can be calculated from equation (3.17), (3.21) and (3.22) respectively.

4.2.6 Calculation of Interaction Parameters for (CO₂-MDEA-H₂O) System

In (CO₂-MDEA-H₂O) system, two neutral species, MDEA and H₂O, and two ionic species, MDEAH⁺ and HCO₃⁻ have been considered in the equilibrated liquid phase. Carbamate formation reaction is not possible because of its bulky nature. In this system, the chemical equilibria involved are already discussed in equations 3.1-3.4 and the corresponding equilibrium constants are already given in equations 4.2-4.5.

The following balance equations for the reacting species can be formed:

Total amine balance:

$$m_t = m_{\text{R R' R'' N}} + m_{\text{R R' R'' N H}^+} \quad (4.16)$$

Carbon dioxide balance:

$$m_t \alpha = m_{\text{CO}_2} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} \quad (4.17)$$

Equation of electroneutrality:

$$m_{\text{H}^+} + m_{\text{R R' R' N H}^+} = m_{\text{OH}^-} + m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} \quad (4.18)$$

For MDEA, R, R' are CH₃ and C₂H₄OH respectively;

Here, m_t indicates total concentration of the amine in all its forms (i.e., the initial, acid-gas-free amine concentration) and α is the loading of the acid gas in question (moles of acid gas per mole of total amine).

The interactions (β_{ij}) of the (CO₂– MDEA–H₂O) system are as follows

$$\begin{aligned} \beta_{\text{R R' R' N H}^+ - \text{R R' R' N}} \\ \beta_{\text{R R' R' N H}^+ - \text{HCO}_3^-} \\ \beta_{\text{R R' R' N} - \text{HCO}_3^-} \end{aligned}$$

With the help of equations 3.1-3.4, 4.2-4.5, 4.10 and 4.22-4.24, the thermodynamic expression of equilibrium partial pressure of CO₂ over aqueous MDEA solutions is as follows,

$$p_{\text{CO}_2} = \frac{H_{\text{CO}_2}}{\Phi_{\text{CO}_2}} \frac{K_4}{K_2} \frac{\gamma_{\text{R R' R' N H}^+}^2 m_{\text{R R' R' N H}^+}^2}{\gamma_{\text{R R' R' N}} m_{\text{R R' R' N}}} \quad (4.19)$$

The value of $m_{R'R'N H^+}$ and $m_{R'R'N}$ can be calculated from equation (3.17) and (3.22) respectively. Φ_{CO_2} can be calculated from (4.23)

4.2.7 Calculation of Fugacity Coefficient

The fugacity coefficients were calculated using the Virial Equation of State.

$$\ln \phi_{CO_2} = \frac{B_{ii}}{RT} \int_0^P dp \quad (4.20)$$

$$\text{or, } \ln \phi_{CO_2} = \frac{B_{ii}P}{RT} \quad (4.21)$$

B_{ii} corresponds to interactions between pairs of molecules and can be calculated from Virial equation of state.

$$\ln \phi_{CO_2} = \frac{B_{ii}P_C}{RT_C} \frac{P_R}{T_R} \quad (4.22)$$

$$\ln \phi_{CO_2} = (B_1 + \omega B_2) \frac{P_R}{T_R} \quad (4.23)$$

Where,

$$B_1 = 0.083 - \frac{0.422}{T_R^{1.6}} \quad (4.24)$$

$$B_2 = 0.139 - \frac{0.172}{T_R^{4.2}} \quad (4.25)$$

Here, P_R and P_C are reduced and critical pressure; T_R and T_C are reduced and critical temperature and ω is the acentric factor it has been taken to be 0.239 for CO_2 . The values considered for P_C and T_C are 73.87 bar and 304.2 K, respectively.

4.3 DEVELOPMENT OF THERMODYNAMIC MODEL FOR THE VAPOUR – LIQUID EQUILIBRIUM OF CO_2 INTO BLENDED ALKANOLAMINE SOLUTIONS

In the aqueous phase for the (CO_2 – blended alkanolamine – H_2O) systems like (CO_2 – MEA – MDEA- H_2O) system the chemical equilibria involved are already discussed in equations 3.26-3.31.

From those reactions, the following equilibrium relations can be written as

$$K_1 = \frac{\gamma_{\text{H}^+}^m \gamma_{\text{OH}^-}^m}{\gamma_{\text{H}^+}^m \gamma_{\text{OH}^-}^m} \quad (4.26)$$

$$K_2 = \frac{\gamma_{\text{H}^+}^m \gamma_{\text{HCO}_3^-}^m}{\gamma_{\text{CO}_2}^m \gamma_{\text{CO}_2}^m} \quad (4.27)$$

$$K_3 = \frac{\gamma_{\text{H}^+}^m \gamma_{\text{CO}_3^{2-}}^m}{\gamma_{\text{HCO}_3^-}^m \gamma_{\text{HCO}_3^-}^m} \quad (4.28)$$

$$K_4 = \frac{\gamma_{H^+}^m \gamma_{H^+}^m \gamma_{R R' R'' N}^m \gamma_{R R' R'' N}^m}{\gamma_{R R' R'' N}^m \gamma_{H^+}^m \gamma_{R R' R'' N}^m \gamma_{H^+}^m} \quad (4.29)$$

$$K_5 = \frac{\gamma_{H^+}^m \gamma_{H^+}^m \gamma_{R R' R' N}^m \gamma_{R R' R' N}^m}{\gamma_{R R' R' N}^m \gamma_{H^+}^m \gamma_{R R' R' N}^m \gamma_{H^+}^m} \quad (4.30)$$

$$K_6 = \frac{\gamma_{HCO_3^-}^m \gamma_{HCO_3^-}^m \gamma_{R R' R'' N}^m \gamma_{R R' R'' N}^m}{\gamma_{R R' R'' N}^m \gamma_{COO^-}^m \gamma_{R R' R'' N}^m \gamma_{COO^-}^m} \quad (4.31)$$

For MEA, R, R' and R'' represent H, H, and C₂H₄OH respectively; for MDEA, R and R' are CH₃ and C₂H₄OH respectively

The following balance equations for the reacting species can be formed:

Total amine balance:

$$m_1 = m_{R R' R'' N} + m_{R R' R'' N H^+} + m_{R R' R'' N COO^-} \quad (4.32)$$

$$m_2 = m_{R R' R' N} + m_{R R' R' N H^+} \quad (4.33)$$

Carbon dioxide balance:

$$m_1 + m_2 = m_{CO_2} + m_{HCO_3^-} + m_{CO_3^{2-}} + m_{R R' R'' N COO^-} \quad (4.34)$$

Equation of electro neutrality:

$$m_{H^+} + m_{R R' R'' N H^+} + m_{R R' N H^+} = m_{OH^-} + m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{R R' R'' N COO^-} \quad (4.35)$$

The vapour pressure of CO₂ is related to the free acid gas concentration in the liquid through Henry's law. Assuming no solvent in the vapour phase, the vapour – liquid equilibrium is given by

$$\Phi_{CO_2} y_{CO_2} P = \gamma_{CO_2} m_{CO_2} H_{CO_2} \quad (4.36)$$

Where, Φ_{CO_2} is the fugacity coefficient, y_{CO_2} is mole fraction, H_{CO_2} is Henry's constant for the acid gas in pure water, P is the total pressure.

4.3.1 Thermodynamic Framework

For the (CO₂ – MEA - MDEA - H₂O) system, the equilibrated liquid phase is assumed to contain three molecular species (H₂O, MEA, and MDEA) and five ionic species (MDEAH⁺, HCO₃⁻, MEAH⁺, DEACOO⁻, and H₃O⁺). Species like free molecular CO₂, OH⁻, and CO₃²⁻ will have a little effect on the observed equilibria (Deshmukh and Mather, 1981). Several previous workers (Li and Mather, 1994, 1996, 1997; Haji-Sulaiman *et al.*, 1996; Posey, 1996) have observed that neglecting the concentrations of free molecular CO₂, and OH⁻ and CO₃²⁻ ions in the liquid phase in this system for CO₂ loading below 1.0 does not result in significant error in the VLE predictions. In our calculation of activity coefficients of the components in the aqueous phase, the activity coefficients of MEA, MDEA, H₂O, MEAH⁺, MDEAH⁺, MEACOO⁻ and HCO₃⁻ are included to account for the non-ideality of the liquid phase. As the free molecular CO₂ concentration in the liquid phase is negligible below the loading of 1.0, the value

of γ_{CO_2} will be close to unity following the unsymmetric normalization of activity coefficient. We can calculate liquid phase molality based on true molecular or ionic species.

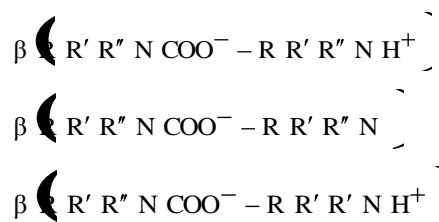
4.3.2 Standard States

In the present work, water is treated as solvent and rest are solute. The activities of the electrolyte and neutral species are defined so that the activity coefficients approach unity in an infinitely dilute solution. The reference state is that of a hypothetical ideal solution of unit molality. On the other hand, the activity coefficient of the solvent approaches unity as the mole fraction of water approaches unity. The reference state is that of pure water at the system pressure and temperature.

4.3.3 Activity coefficient model

In this work both water MDEA and MEA are treated as solutes. The standard state associated with solvent is the pure liquid at the system temperature and pressure. The adopted standard state for ionic solutes is the ideal, infinitely dilute aqueous solution (infinitely dilute in solutes and alkanolamines) at the system temperature and pressure. The reference state chosen for molecular solute CO_2 is the ideal, infinitely dilute aqueous solution at the system temperature and pressure.

The interactions (β_{ij}) considered in blended alkanoamine systems are



$$\begin{aligned}
& \beta \left(\text{R}'\text{R}''\text{N COO}^- - \text{R}'\text{R}'\text{R}'\text{N} \right) \\
& \beta \left(\text{R}'\text{R}''\text{N H}^+ - \text{R}'\text{R}'\text{R}'\text{N} \right) \\
& \beta \left(\text{R}'\text{R}'\text{R}''\text{N H}^+ - \text{HCO}_3^- \right) \\
& \beta \left(\text{R}'\text{R}''\text{N H}^+ - \text{R}'\text{R}'\text{R}'\text{N} \right) \\
& \beta \left(\text{R}'\text{R}'\text{R}''\text{N} - \text{HCO}_3^- \right) \\
& \beta \left(\text{R}'\text{R}''\text{N} - \text{R}'\text{R}'\text{R}'\text{N H}^+ \right) \\
& \beta \left(\text{R}'\text{R}'\text{N H}^+ - \text{R}'\text{R}'\text{R}'\text{N} \right) \\
& \beta \left(\text{R}'\text{R}'\text{R}'\text{N H}^+ - \text{HCO}_3^- \right) \\
& \beta \left(\text{R}'\text{R}'\text{R}'\text{N} - \text{HCO}_3^- \right)
\end{aligned}$$

where, $\text{R}'\text{R}'\text{R}''\text{N}$ and $\text{R}'\text{R}'\text{R}'\text{N}$ indicate MEA and MDEA respectively

After simplification from equations (3.26)-(3.31), (4.27) - (4.43), the thermodynamic expression for equilibrium partial pressure of the (MEA+MDEA+ CO_2 + H_2O) system is as follows

$$\begin{aligned}
p_{\text{CO}_2} = \frac{H_{\text{CO}_2}}{\Phi_{\text{CO}_2}} & \left(\frac{K_4 \gamma_{\text{R}'\text{R}'\text{R}''\text{N H}^+} m_{\text{R}'\text{R}'\text{R}''\text{N H}^+}}{\gamma_{\text{R}'\text{R}'\text{R}''\text{N}} m_{\text{R}'\text{R}'\text{R}'\text{N}}} + \frac{K_5 \gamma_{\text{R}'\text{R}'\text{R}'\text{N H}^+} m_{\text{R}'\text{R}'\text{R}'\text{N H}^+}}{\gamma_{\text{R}'\text{R}'\text{R}'\text{N}} m_{\text{R}'\text{R}'\text{R}'\text{N}}} \right) \\
& \left(\frac{K_6 \gamma_{\text{R}'\text{R}'\text{R}''\text{N COO}^-} m_{\text{R}'\text{R}'\text{R}''\text{N COO}^-}}{K_2 \gamma_{\text{R}'\text{R}'\text{R}''\text{N}} m_{\text{R}'\text{R}'\text{R}'\text{N}}} \right) \quad (4.37)
\end{aligned}$$

Φ_{CO_2} can be calculated from equation (4.23), $m_{\text{R R}' \text{R}'' \text{N H}^+}$, $m_{\text{R R}' \text{R}'' \text{N}}$, $m_{\text{R R}' \text{R}' \text{N H}^+}$, $m_{\text{R R}' \text{R}' \text{N}}$ and $m_{\text{R R}' \text{R}'' \text{N COO}^-}$ can be calculated from equation (3.45), (3.48), (3.46), (3.49) and (3.47) respectively.

4.4 METHOD OF SOLUTION

In this work the solubility data of CO_2 in aqueous alkanolamine solutions of various concentrations, in a wide range of CO_2 partial pressure and temperatures and below a CO_2 loading of 1.0 mol CO_2 /mol amine, have been used to estimate the interaction parameters by regression analysis. The best values of the interaction parameters were determined by data regression using the available solubility data, most of which were measured at moderate to high acid gas loadings. Since the interaction parameters are characteristic of pair interactions of components of the solution and are independent of solution composition, the fitted parameters are valid outside the range of concentrations over which they were fitted. Hence, the VLE model itself is valid at low acid gas partial pressures even though the parameters of the activity coefficient model were not fitted in this range.

In the ternary (CO_2 -alkanolamine-water) system, in principle, there are a large number of binary interaction parameters. However, because many of the species are present in the liquid phase at low or negligible concentrations, parameters associated with them do not significantly affect the representation of VLE of acid gas-aqueous alkanolamine system.

At first all available experimental data from different authors were used for regression analysis to obtain the interaction parameters, which resulted in a large average correlation deviation. Then a lot of equilibrium curves were made at the same temperatures and the same initial amine concentrations but from the

different authors and some sets of data, which were far away from most of the data were discarded. The method of Weiland *et al.* (1993) (The predictions of zero-interaction model are closely approximating the data themselves) to discard some of the bad sets of data was also used. Finally, the combination of data useful for generating a correlation to obtain a set of interaction parameters has been identified. The objective function used for optimization is given by equation (4.38)

$$F = \sum \left| \left\{ \left(p_{\text{CO}_2} \right)_{\text{cal}} - \left(p_{\text{CO}_2} \right)_{\text{exp}} \right\} \left(p_{\text{CO}_2} \right)_{\text{exp}} \right| \quad (4.38)$$

We seek the numerical values of interaction parameters that will minimize the difference between the measured values of equilibrium partial pressure of CO₂ over alkanolamine solutions and the values calculated from the model. The objective function chosen in this work takes care of giving uniform weightage throughout the entire range of partial pressure (from low to high), provided the data scatter throughout the entire range of partial pressure (from low to high) is, as claimed in the concerned literature, is more or less uniform.

One of the primary goals of a modeling effort of this nature is to provide a means to confidently interpolate between and extrapolate beyond reported experimental data. The confidence that is placed in interpolation and extrapolation (prediction) with the model is dependent on both correct model formulation and the quality of the data used to fit parameters of the model.

The problem of parameter estimation for the model to predict the VLE of an acid gas-aqueous alkanolamine system involves regression of literature data to get the optimum values of the interaction parameters. Owing to the presence of multiple solutions some approaches were unable to obtain the global solution for the general equilibrium problem because they could not jump over the local

minima. ‘*fmincon*’ function, which is a constrained optimization function using quasi-Newton and Sequential Quadratic Programming (SQP) methods, has been used here for minimization of the proposed objective function with variable bounds.

4.5 RESULTS AND DISCUSSIONS

For the (CO_2 – MEA - H_2O) system, the interaction parameters were determined using 3.75 and 5 M alkanolamine solution of CO_2 at 25, 40, 60, 80 and 100 °C over 70 data points and in the partial pressure range of CO_2 of 1-10000 kPa. The literature data has been taken from Lee and Mather (1976) and model equation 4.15 was used. The average absolute percentage deviations between the experimental and model correlated CO_2 partial pressure (%AAD correlation) is 34 and interaction parameters are listed in Table 4.2. The model predictions are in good agreement with the literature data over a wide temperature, amine composition and CO_2 partial pressure as depicted in Table 4.6.

For the (CO_2 – DEA - H_2O) system, the model equation 4.15 was used to determine the interaction parameters and the literature value were taken from Lee and Mather (1972) using 3 and 5 M alkanolamine solution of CO_2 at 25, 40, 60, 80 and 100 °C over 48 data points in the partial pressure range of CO_2 is 2.17-687 kPa. The correlation results are in good agreement with the experimental data with an average absolute percentage deviations of correlation is 28.4 and interaction parameter values are listed in Table 4.3. The model predictions are in reasonable agreement with data available in the open literature and are listed in Table 4.7.

For the (CO_2 – MDEA - H_2O) system, the model equation 4.25 was used to determine the interaction parameters and the literature value taken from Shen

& Li (1992) using 30 wt% alkanolamine solution of CO₂ at 40, 60, 80 °C over 19 data points and interaction parameter values are listed in Table 4.4.

For the (CO₂ – MEA - MDEA - H₂O) system, the model equation 4.37 was used and the interaction parameters for the (CO₂ – MEA - H₂O) system and (CO₂ – MDEA - H₂O) system were used here for the blended amine model. In this mixed alkanolamine system, remaining interaction parameters were determined by regression analysis using the solubility data of CO₂ in 12 wt % MEA + 18 wt% MDEA aqueous solutions at 40, 60, 80 and 100 °C (Shen and Li ,1993) and are listed in Table 4.5 . The prediction results are in good agreement with the experimental data with an average absolute percentage deviations of 29.6 as presented in Table 4.8

4.6 CONCLUSION

The rigorous thermodynamic model developed in this work used two types of equilibria; phase equilibria and chemical reaction equilibria. The vapor phase non-ideality had been taken care of in terms of fugacity coefficient calculated using Virial Equation of State. The activity based model was developed using extended Debye- Hückel theory of electrolytic solution with short range, non-electrostatic interactions. For (CO₂ – MEA - H₂O), (CO₂ – MDEA - H₂O) and (CO₂ – DEA - H₂O) systems, the interaction parameters were estimated, which accounted for the liquid phase non-ideality. The equilibrium constants were taken from literature and were functions of temperature only. The neutral and ionic species present in the equilibrated liquid phase were estimated with zero interaction model and incorporated. In this way, the regression function was used to estimate a fewer parameters (only interaction parameters) in comparison to the Deshmukh Mather model, where the individual species concentrations along with the interaction parameters were also regressed. For the mixed amine system, the interaction parameters from single amine solutions were used and the additional

parameters for the ternary system were regressed using the ternary VLE data. From the correlation and prediction deviation, it appears the model prediction error is little high in comparison to the approximate model developed by us, yet the significance of the developed rigorous thermodynamic model cannot be over ruled. There remains a necessity of refinement of the developed rigorous model in terms of the accurate speciation, i.e., exact determination of the species concentration in the equilibrated liquid phase and use of better optimization algorithm, may be non-traditional one, which will ensure global minima.

Table 4.1 Temperature dependence of the equilibrium constants and Henry's constant.

$$\ln K_i = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T$$

$$\ln H_{\text{CO}_2} = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T$$

Reaction	comp	C ₁	C ₂	C ₃	C ₄	Ref
3.2, 3.27	CO ₂	235.482	-12092.1	-36.7816	0	^d
3.4, 3.28	DEA (deprotonation)	-6.7936	5927.65	0	0	^a
3.5, 3.30	DEA (decarbamation)	4.5416	-3417.34	0	0	^a
3.4, 3.28	MEA (deprotonation)	2.121	-8189.38	0	-0.007484	^b
3.5, 3.30	MEA (carbamate reversion)	2.8898	-3635.09	0	0	^b
3.4, 3.29	MDEA (deprotonation)	-56.27	-4044.8	7.848	0	^c
3.14	H _(CO2)	94.4914	-6789.04	-11.4519	-0.010454	^d

^a Austgen *et al.*, 1989; ^b Li & Mather, 1994; ^c Posey, 1996; ^d Edwards *et al.*, 1978

Table 4.2 Interaction parameters of (CO₂ – MEA– H₂O) system

MEA (molality)	Binary Pair of (CO ₂ +MEA + H ₂ O) system	Kg/mol	%AAD correlation
3.75, 5	$\beta \left(R' R'' N COO^- - R' R' R'' N H^+ \right)$	0.0512939	34
	$\beta \left(R' R'' N COO^- - R' R' R'' N \right)$	0.293549	
	$\beta \left(R' R' R'' N H^+ - HCO_3^- \right)$	-0.089612	
	$\beta \left(R' R'' N - R' R' R'' N H^+ \right)$	-0.093986	
	$\beta \left(R' R' R'' N - HCO_3^- \right)$	0.195222	

Reference- Lee, Otto & Mather (1976); Temperature -298K, 313K, 333K, 353K, 373K; No of data points-70; Partial pressure range- 1-10000 kPa

Table 4.3 Interaction parameters of (CO₂ – DEA– H₂O) system

DEA (molality)	Binary Pair of (CO ₂ +DEA + H ₂ O) system	Kg/mol	%AAD correlation
3.5, 5	$\beta \left(R' R'' N COO^- - R' R' R'' N H^+ \right)$	0.120857	28.4
	$\beta \left(R' R'' N COO^- - R' R' R'' N \right)$	0.314057	
	$\beta \left(R' R' R'' N H^+ - HCO_3^- \right)$	-0.085265	
	$\beta \left(R' R'' N - R' R' R'' N H^+ \right)$	-0.207674	
	$\beta \left(R' R' R'' N - HCO_3^- \right)$	0.194998	

Reference- Lee, Otto & Mather (1972); Temperature -298K, 313K, 333K, 353K, 373K; No of data points-48; Partial pressure range- 2.17- 687 kPa

Table 4.4 Interaction parameters of (CO₂ – MDEA– H₂O) system

MDEA (molality)	Binary Pair of (CO ₂ +MDEA + H ₂ O) system	Kg/mol	%AAD correlation
2.52	$\beta \left(\text{R R' R' N H}^+ - \text{R R' R' N} \right)$	0.048129	32.1
	$\beta \left(\text{R R' R' N H}^+ - \text{HCO}_3^- \right)$	-0.001999	
	$\beta \left(\text{R R' R' N} - \text{HCO}_3^- \right)$	0.012999	

Reference- Shen & Li (1992); Temperature - 313K, 333K, 353K; No of data points- 19; Partial pressure range- 1.2 - 1197 kPa

Table 4.5 Interaction parameters of (CO₂ – MEA–MDEA- H₂O) system

MEA (molality)	MDEA (molality)	Binary Pair of (CO ₂ +MEA + MDEA+H ₂ O) system	Kg/mol	%AAD correlation
1.964	1.511	$\beta \left(\text{R}' \text{R}'' \text{N COO}^- - \text{R}' \text{R}' \text{R}'' \text{N H}^+ \right)$	0.0512939	38.3
		$\beta \left(\text{R}' \text{R}'' \text{N COO}^- - \text{R}' \text{R}' \text{R}'' \text{N} \right)$	0.293549	
		$\beta \left(\text{R}' \text{R}' \text{R}'' \text{N H}^+ - \text{HCO}_3^- \right)$	-0.089612	
		$\beta \left(\text{R}' \text{R}'' \text{N} - \text{R}' \text{R}' \text{R}'' \text{N H}^+ \right)$	-0.093986	
		$\beta \left(\text{R}' \text{R}' \text{R}'' \text{N} - \text{HCO}_3^- \right)$	0.195222	
		$\beta \left(\text{R}' \text{R}' \text{R}' \text{N H}^+ - \text{R}' \text{R}' \text{R}' \text{N} \right)$	0.048129	
		$\beta \left(\text{R}' \text{R}' \text{R}' \text{N H}^+ - \text{HCO}_3^- \right)$	-0.001999	
		$\beta \left(\text{R}' \text{R}' \text{R}' \text{N} - \text{HCO}_3^- \right)$	0.012999	
		$\beta \left(\text{R}' \text{R}'' \text{N COO}^- - \text{R}' \text{R}' \text{R}' \text{N H}^+ \right)$	1.510383	
		$\beta \left(\text{R}' \text{R}'' \text{N COO}^- - \text{R}' \text{R}' \text{R}' \text{N} \right)$	0.006196	
		$\beta \left(\text{R}' \text{R}'' \text{N H}^+ - \text{R}' \text{R}' \text{R}' \text{N} \right)$	0.445696	
		$\beta \left(\text{R}' \text{R}'' \text{N} - \text{R}' \text{R}' \text{R}' \text{N H}^+ \right)$	0.419807	

Reference- Shen & Li (1992); Temperature - 313, 333, 353, 373K; No of data points – 43; Partial pressure range- 0.9 - 1998 kPa

Table 4.6 The VLE prediction for (CO₂ – MEA – H₂O) system

Reference	MEA (molality)	Temp (K)	Data points	CO ₂ Partial pressure range (kPa)	^a AAD% Prediction
Lee, Otto and Mather (1976)	2.5	298, 313, 333, 353, 373	35	0.1 - 1000	32.3
Lee, Otto and Mather (1976)	1.0	298, 313, 333, 353, 373	26	0.316 - 316	44.1
Shen and Li (1992)	4.9	313, 333, 353, 373	46	1.1-1975	35.8
Jones <i>et al</i> (1959)	2.5	313	5	2.0 – 120.7	34.8
Lee <i>et al</i> (1976)	2.5	313	4	10 – 316	35.3
Shen and Li (1992)	2.5	313	7	15.7- 563	12.6
Lawson and Grast(1976)	2.5	313, 333, 353	5	59.2 – 238.2	46.8

Table 4.7 The VLE prediction for (CO₂ – DEA – H₂O) system

Reference	DEA (molality)	Temp (K)	Data points	CO ₂ Partial pressure range (kPa)	^a AAD% Prediction
Lee, Otto and Mather (1972)	3.5	298, 313, 333, 353, 373	24	2.17 - 687	32
Lee, Otto and Mather (1972)	5.0	298, 313, 333, 353, 373	24	0.316 - 316	24.9
Lawson and Grast(1976)	2.4	310, 339, 353, 366	21	1.97 - 2276	31.3
Seo and Hong (1996)	2.85	313, 333, 353	15	4.85 – 357.3	39.1
Kennard and Meisen (1984)	4.2	373	6	93 - 3742	35.3

Table 4.8 The VLE prediction for (CO₂ – MEA – MDEA - H₂O) system

Reference	MEA (molality)	MDEA (molality)	Temp (K)	Data points	CO ₂ Partial pressure range (kPa)	^a AAD% Prediction
Shen and Li (1992)	3.928	0.504	313, 333, 353, 373	42	1.5 - 1981	29.6

$$^a \text{AAD\%} = \left[\sum_n \frac{|p_{\text{cal}} - p_{\text{exp}}|}{p_{\text{exp}}} \right] / n \times 100$$

Chapter 5

FUTURE WORK AND RECOMMENDATION

Chapter 5

FUTURE WORK AND RECOMMENDATION

The approximate thermodynamic models developed in this work have shown remarkable correlation and prediction ability. The rigorous thermodynamic models developed of course need some refinements to perform in a better way so far its correlation and prediction ability is concerned. No compromises were done so far as the degree of thermodynamic rigour is concerned in building the model but its solution part demands serious consideration. A thorough introspection reveals that the future course of this particular work should proceed as follows,

1. The interaction parameters of free CO_2 with the ionic and molecular species present in equilibrium liquid phase have to be considered in the rigorous thermodynamic model. This incorporation in the activity model will enable the model to predict accurately near the loading of almost 1.0 or even greater.
2. From the measurement of pH and conductivity of CO_2 loaded alkanolamine solution the model refinement is possible.

3. The neutral and ionic species present in the equilibrated liquid phase were estimated with zero interaction model and directly incorporated in the developed model. The accurate speciation, i.e., exact determination of the species concentration in the equilibrated liquid phase is necessary so that the developed model can function properly and in a more precise way.
4. The parameter estimation for the present phase + chemical equilibrium model used gradient based traditional optimization algorithms. It has been observed that many times the optimal solution (minimal here) is trapped in to a local minima in the vector search space. The use of nontraditional optimization algorithm for parameter estimation, perhaps, will bring a considerable improvement in the solubility prediction by ensuring global minima.
5. In this work rigorous thermodynamic model has been developed to predict the VLE of CO₂ in alkanolamines. It is recommended that the model be extended to represent VLE of other gases as well, e.g., COS and CS₂, which also are often present in the sour gas streams. This is a logical step towards developing a generic model for vapour-liquid equilibrium of acid gases into alkanolamines.

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